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16. ABSTRACT

The objective of this symposium was to provide a forum for the statement of the state-of-the-art in sampling, analysis, and quality assurance of the oil shale industry pollutants. Opinions from governmental and industrial research organizations were solicited as to the future needs in these areas.

The symposium was held March 26-28, 1979 in Denver, Colorado. 260 registered attendees were present. Papers from industry, government, and academic researchers were presented and discussed. This is a report of the proceedings at the symposium.

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SAMPLING, ANALYSIS AND QUALITY ASSURANCE
MARCH 1979

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FOREWORD

When energy and material resources are extracted, processed converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report contains the proceedings of the Oil Shale Symposium: Sampling, Analysis, and Quality Assurance sponsored by IERL-Ci which met in Denver, Colorado, March 26-28, 1979. The presented papers discussed the experiences of researchers in the chemical, biological, and physical sciences that apply to oil shale sampling analysis, and quality assurance. This report will serve as a state-of-the-art guide to those who are involved in oil shale related endeavors, a large and rapidly growing group. For further information contact the Branch of Oil Shale and Energy Mining, Energy Pollution Control Division (IERL-Ci).

David G. Stephan
Director,
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

This report presents the papers given at the IERL-Ci "Oil Shale Symposium: Sampling, Analysis, and Quality Assurance," March 26-28, 1979, Denver, Colorado.

This symposium brought together expert scientists from a variety of disciplines, their papers present methodologies for pollution analysis relevant to the oil shale industry. Cooperation and information exchange among academic, industrial, and governmental researchers were prime objectives.

Topics discussed include: pollutants which can and should be characterized and quantified, media to be examined, health effects, sampling and analysis methods, quality assurance needs, future directions of methodology, reference materials, and instrumentation development. Opinions from governmental, industrial, and academic researchers concerning the future needs in these areas are presented.

This report was submitted in fulfillment of Grant No. R806156 by Denver Research Institute under the partial sponsorship of the United States Environmental Protection Agency. This report covers a period from September, 1978, to October, 1979. Work was completed as of February 15, 1980.

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The cooperation of each author who presented the results recorded in these proceedings is gratefully acknowledged. The efforts of the many technical reviewers who selected these papers and made suggestions for improvements were appreciated. The session leaders kept the program on schedule while allowing for stimulating, thought-provoking discussion periods following each presentation.

By presenting some of the most current work in oil shale environmental studies, the symposium attracted a large audience from the national and international scientific community. The organizers and participants were jointly responsible for the success of the symposium.

QUALITY ASSURANCE AND POLLUTION CONTROL TECHNOLOGY RESEARCH

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Pollution is a fact of life.

It's an undesirable consequence of both natural and manmade processes.

What can we do to prevent or control pollution, rather than clean up after it has occurred?

Our goals should be to minimize the environmental impact which may be caused by development of the oil shale industry, and to do this with a minimum of economic impact.

We need to confirm the effectiveness and applicability of pollution control concepts. And we need to prove that the extraction processes used will not have any unmanageable adverse effects.

It is the responsibility of EPA's Industrial Environmental Research Laboratories to develop and demonstrate new and improved pollution control technology that will help us meet our nation's energy needs. To accomplish this, research must conform to the highest quality assurance standards. Sampling and analytical services are an important aspect of most research and demonstration projects. Decisions of both technical and economic importance are made based on the data generated by these sampling and analytical programs.

The development and testing of effective pollution control equipment is the product of the efforts of scientists and engineers, working together within social, economic, and regulatory constraints.

The pollution control technology now available may be capable of doing the job we need for oil shale development. But the effective use and advancement of that technology depends upon our ability to communicate meaningful data as the basis for evaluations. At each step in the research process we must have a commitment not only to exchange information, but to assure the accuracy, reliability, and overall quality of our information.

Pollution control research requires a series of measurements. These include:

- Measurements to define and describe the pollutant.

- A measurement of the extent of pollution, and a measurement of the effectiveness of controls in reducing pollution.

The key word is measurement. Scientists provide procedures for measuring the physical, chemical, and biological parameters which characterize pollution problems and solutions. Pollution control technology researchers use these measurements to devise techniques and equipment that can reduce pollution. This research is dependent on the quality of measurements if effective controls are to be developed.

Quality Assurance encompasses all actions taken by an organization to achieve accurate and reliable research results. An established Quality Assurance program is essential for any organization to produce valid sampling and analytical data.

Quality Assurance is an integral part of the management of a total research system. Since decisions are made from the data, and the data come from samples, it is essential that the procedures for sample collection, handling, analysis, and data interpretation be trustworthy.

But in addition to accurate, reliable information and the right equipment, the positive attitudes of people who know what they're doing is essential.

We need your commitment toward the planning, development, and application of the appropriate control technology for oil shale development.

To achieve this will require an interactive, cooperative approach.

One example is this Oil Shale Symposium. Many of you in the audience are acknowledged experts. You can present the state-of-the-art in methodologies; you can help define research problems, and establish directions for future research. For this effort, cooperation and information exchange among all researchers is the prime objective.

We must openly discuss the problems facing us, and be aware of what is currently being done. It is in everyone's interest to work together to establish and verify methodologies, collect data, exchange information, and assure the quality of scientific research.

It is imperative that we cooperate to assure the nation develops our vital resources in a manner which is economically viable and environmentally sound.

EPA'S QUALITY ASSURANCE PROGRAM FOR WATER AND WASTE ANALYSIS

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ABSTRACT

The paper has described EPA's Quality Assurance program for water and waste analyses of all parameters required under the present environmental legislation. The program includes:

1. Development of manuals and guidelines for quality control, sampling, sample preservation and other support needs,
2. Distribution of quality control check samples,
3. Maintenance of a permanent repository for priority pollutants and all other trace organics of interest to the agency,
4. Conduction of formal studies to validate selected methodology,
5. Conduction of formal evaluation studies of laboratory performance and determination of acceptance for approval or formal certification, and
6. Operation of a formal equivalency program for approval of alternate test procedures as required under the FWPCA Amendments and the National Interim Primary Drinking Water Regulations.

INTRODUCTION

Measurements of environmental samples are used in the assessment of health effects, the setting of environmental standards and guidelines, and the enforcement of environmental regulations. EPA established a quality assurance program to assure that these measurements are reliable, and hence, legally defensible, through development and implementation of uniform quality control procedures.

Table 1 describes responsibilities for quality assurance in EPA. Program management was assigned to the Office of Research and Development for uniform application of the same criteria in a national program. However, the technical responsibility was divided into three analytical areas of air, water, and radiation analyses because the methods of sample collection and analyses differ, the relevant laws or sections of laws differ, and the time tables for regulation differ for each area.

TABLE 1. QUALITY ASSURANCE PROGRAM IN EPA

Program Management	Office of Monitoring & Technical Support ORD, Washington, DC 20460
Radiation	Environmental Monitoring & Support Laboratory Environmental Research Center Las Vegas, NV 89109
Air	Environmental Monitoring & Support Laboratory Environmental Research Center Research Triangle Park, NC 27711
Water	Environmental Monitoring & Support Laboratory Environmental Research Center Cincinnati, OH 45268
Regional Coordination	Ten Regional Quality Assurance Coordinators

In addition, each Regional Administrator in EPA designated one person, the Regional Quality Assurance Coordinator, to be the focal point for all quality assurance activities in the Federal, state and local agencies under his regional jurisdiction. The only change, as QA activities have expanded, has been appointment of separate coordinators for air analyses and water analyses in some regions.

QUALITY ASSURANCE PROGRAM

The Quality Assurance Program for water and wastewater analyses assigned to the Environmental Monitoring and Support Laboratory at Cincinnati (EMSL-CI) has five major functions as shown in Table 2.

Manuals and Guidelines

EMSL-CI has developed the guidance for quality control in sampling, sample preservation, laboratory operations and analyses. EMSL-CI has also provided the technical support necessary for selection of methodology and quality assurance required under the Certification program for water supply laboratories.

TABLE 2. EPA'S QUALITY ASSURANCE PROGRAM FOR WATER/WASTEWATER ANALYSES

1. Development of Manuals and Guidelines.

   Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EMSL-CI, 1979.

   Sampling and Sample Preservation Manual, EMSL-CI, in preparation.

   Input to: Manual for Interim Certification of Laboratories involved in Analyzing Public Water Supplies, Office of Drinking Water, 1978.

2. Provision of Quality Control Check Samples to within-laboratory Quality Assurance Programs for all parameters under the laws.

3. Conduction of formal method validation studies for all parameters under the laws.

4. Conduction of Performance Evaluation Studies for laboratory approval and/or formal certification for all parameters under the laws.

5. Equivalency of Alternate Test Procedures.

Reference-Type Samples

The Quality Assurance Program for water and wastewater analyses uses reference-type samples for all of its activities in method selection, method validation, intralaboratory quality control, performance evaluation and certification. The samples are used as knowns in intralaboratory quality control activities or as unknowns in interlaboratory evaluations and method studies.

The EPA samples are prepared as concentrates in Youden pairs[1] using water or an organic liquid as solvent. Exact amount of high purity chemicals are weighed, dissolved and brought to volume wIth ultrapure water or other pure solvent to form the sample concentrate containing multiple parameters. The analyst in the user-laboratory dilutes the sample concentrates to volume according to instructions, to produce samples with established True Values. The "true value" concept is a key factor in EPA's sample design because it permits the establishment of accuracy and precision. Bias and interference are then measured by comparison of the recoveries of identical spikes into laboratory-pure and natural water or wastewater.

USES OF THE REFERENCE-TYPE SAMPLES

Quality Control Samples

Quality Control (QC) samples are furnished without charge to interested governmental, industrial, commercial, and private laboratories for use as secondary checks on their within-laboratory quality control programs. The samples are intended as independent measures of technique and performance, not as replacements for the standards, replicates or spike samples run routinely as part of the laboratory's own QC program.

There is no certification or other formal evaluative function resulting from the use of QC samples. No reports are prepared and there is no requirement for use of specific methodology in these QC analyses.

Method Validation Studies

The Environmental Monitoring and Support Laboratory conducts formal interlaboratory studies to evaluate methods selected by EPA for its manuals such as: Methods for Chemical Analysis of Water and Wastes, Biological Field and Laboratory Methods for Measuring the Quality of Surface Waters and Effluents, and Microbiological Methods for Monitoring the Environment, Water and Wastes. Federal, state, local, and industrial laboratories take part in these roundrobin studies which carry deadlines and conclude with preliminary reports distributed to all participants and formal study reports prepared thereafter. In these reports, laboratories are identified only by code number.

Performance Evaluation Studies

In this second type of interlaboratory study, samples are used as unknowns to measure laboratory performance. Analytical results are rated acceptable/nonacceptable as judged against preestablished performance limits and the ratings are used by EPA programs for informal accreditation and legally-required certification of laboratories.

Sample Types and Parameters

The chemical, biological and microbiological parameters in the Quality Assurance Program respond to the three water laws, to energy-related water monitoring needs and to the impact of the Toxic Substances Control Act and Resource Conservation and Recovery Act on the water laws.

Except for natural materials (solids, chlorophyll and petroleum hydrocarbons, etc.), the reference samples are prepared as concentrates in sealed glass ampuls. When diluted to volume with distilled or natural water, according to instructions, the concentrations of constituents range from minimal detectable levels to those found in heavily polluted streams.

Available Quality Control Samples for Water Quality Analyses

Demand Analyses--BOD, COD, TOC

Mineral/Physical Analyses--sodium, potassium, calcium, magnesium, pH, sulfate, chloride, fluoride, alkalinity/acidity, total hardness, total dissolved solids, and specific conductance

Mercury--organic and inorganic

Trace Metals--aluminum, arsenic, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, selenium, vanadium, and zinc

Cyanide--simple and complex

Total Nonfilterable, Total Filterable, and Total Volatile Residue

Linear Alkylate Sulfonate--LAS, the anionic surfactant standard required for the MBAS Test

Nitrilotriacetic Acid--phosphate substitute for detergents

Chlorophyll--spectrophotometric analyses

Chlorophyll--fluorometric analyses

Petroleum Hydrocarbons--two crude oils, #2 fuel oil and Bunker C, for characterization analyses

Pesticides--aldrin, dieldrin, DDT, DDE, DDD, heptachlor, chlordane

Polychlorinated Biphenyls--Aroclor 1254 and 1016

Volatile Organics--six-nine compounds, including THM's

Available Quality Control Samples for Drinking Water Analyses

Nitrate/Fluoride

Trace Metals--arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver

Herbicides--2-4D, 2,4,5-TP

Pesticides--Endrin, lindane, methoxychlor, toxaphene

Turbidity

Sample Types in Preparation:

- Phthalate Esters
- Haloethers
- Chlorinated Hydrocarbons
- Nitrobenzenes/Isophorone
- Nitrosamines
- Benzidines
- Phenols (specific)
- Polynuclear Aromatics
- Pesticides/PCBs
- Purgeables
- Acrolein, Acrylonitrile
- Cyanide
- Antimony, Silver and Thallium
- Residual Chlorine
- Oil and Grease
- Trihalomethanes
- Phenol--4AAP Method
- Microbiology--Quantitative Samples
- Aquatic Biology--Diatom, plankton, periphyton and macroinvertebrate samples

REPOSITORY

In 1979, a permanent EPA repository was established by EMSL-Cincinnati to provide calibration standards and other pure organic compounds to EPA, other Federal, state and local laboratories as required under the water and wastewater regulations. The first series to be prepared will be 114 priority pollutants, but the repository will be expanded to include other toxic compounds and trace organics of interest to the Agency.

EQUIVALENCY

An added program function in Quality Assurance, Equivalency, is based on the practical needs of the regulations. Both the Federal Water Pollution Control Act Amendments and the Safe Drinking Water Act regulations specify analytical methodology but recognize a need for adjustment in the use of methods and the development of new methodology. This adjustment is described under the Alternate Test Procedure mechanism of the regulations.[2 3 4] If an industry, permittee or water treatment facility has a methodology or instrument which produces results equivalent to the specified methodology, the applicant is given an opportunity to provide analytical data to prove this equivalency and obtain approval for use of the Alternate Test Procedure (ATP) to satisfy requirements under the law.

There are two types of Alternate Test Procedure (ATP) approval based on the extent of method use:

1. Limited Use--Requests for limited use applications may be initiated by a discharger, water utility or by a private, state or EPA regional laboratory for use within that region or state. The proposed alternate method is forwarded to the appropriate State Director or EPA Regional Administrator. If the state and regional review determines the proposed method is unacceptable, the application may be denied and the applicant notified. If the application appears acceptable it is forwarded to the Director, EMSL-CI for a technical review and recommendation. EMSL-CI has at this time three options: 1) recommend approval, 2) recommend denial, or 3) request

additional information. Recommendations for approval or denial are based on the technical information supplied with the application, statistical review of data submitted, and external technical review. Applications for approval of alternate procedures for radiochemical analyses are sent for review to the Environmental Monitoring and Support Laboratory --Las Vegas and applications for drinking water analyses are sent for review to the Municipal Environmental Research Laboratory--Cincinnati.

2. Nationwide Use--This broad approval is a mechanism available to instrument and analytical system manufacturers to permit use of an alternate test procedure by any person to monitor effluents or water supply samples in the program where approval has been granted. Applications for nationwide use of ATP are sent to the Director, EMSL-CI.

Requirements of Proposals for Alternate Methodology-The proposer of an alternate method must provide:

1. A detailed writeup of the analytical method.
2. Literature references supporting the alternate test method.
3. Satisfactory analytical data comparing the approved method and the alternate method on the specific waters or wastewaters to which the alternate method will be applied.

In first considering the application, the reviewer will consider whether approval is needed under the law. The proposed method may simply be a permissible option to the approved method. If judged an alternate method by the reviewer, he will examine the data provided with the request to determine if there is sufficient comparative data and if the data support the alternate procedure. The reviewer will then approve or disapprove the ATP sufficiency and acceptability of the data. If additional data are required, there are specific test protocols for limited use and nationwide use, as shown in Tables 3 and 4.

TABLE 3. DATA REQUIREMENTS FOR LIMITED USE
APPROVAL OF ALTERNATE TEST PROCEDURE

1. Sources--One for permit holder or drinking water system. Five for state or regional use.
2. Three samples from each source.

3. Four replicate analyses each by the proposed and approved method.

$$\frac{\text{Sources}}{1\text{-}5} \text{ X } \frac{\text{Samples}}{3} \text{ X } \frac{\text{Replicates}}{4} \text{ X } \frac{\text{Methods}}{2} = \frac{\text{Total Analyses}}{24\text{-}120}$$

TABLE 4. DATA REQUIREMENTS FOR NATIONWIDE APPROVAL OF ALTERNATE TEST PROCEDURES

1. Five Industrial (Discharge) Sources Identified by Standard Industrial Classification (SIC) Code or Five Drinking Water Sources.
2. Six samples from each source.
3. Four replicate analyses each, by the proposed and approved method.

$$\frac{\text{Sources}}{5} \text{ X } \frac{\text{Samples}}{6} \text{ X } \frac{\text{Replicates}}{4} \text{ X } \frac{\text{Methods}}{2} = \frac{\text{Total Analyses}}{240}$$

Statistical Testing--For applications involving the submission of comparability data, the Equivalency Staff applies statistical techniques to the data as shown in Table 5.

TABLE 5. STATISTICAL PROTOCOL FOR APPROVAL OF ALTERNATE TEST PROCEDURES

1. Calculate mean and standard deviation.
2. Test for outliers.
3. Check distribution for normality.
4. Test for equality among within-sample standard deviations.
5. Test for equality of pooled within-sample variance.
6. Test for equality of method means.
7. Conclusions.

Final Approval--The final approving authority for limited use application resides with the EPA Regional Administrator. Nationwide approval for the National Pollutant Discharge Elimination System (NPDES) analyses resides with the Assistant Administrator, Office of Research and Development, EPA Headquarters. National Interim Primary Drinking Water Regulations (NIPDWR) nationwide approvals are made by the Deputy Assistant Administrator, Office of Drinking Water, EPA Headquarters. Notification of nationwide approval will be made in the Federal Register, and in EPA's Quality Assurance Newsletter, published quarterly by EMSL-Cincinnati. Approval or denial of the ATPs is based on the regional review and the technical review and recommendation of EMSL-Cincinnati.

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EPA REGULATORY/RESEARCH PROGRAM

T. Thoem, A. Christianson, E. Harris,
E. Bates and W. McCarthy
U.S. Environmental Protection Agency

ABSTRACT

Legislation in the form of the Clean Air Act, the Clean Water Act, the Safe Drinking Water Act, and the Resource Conservation and Recovery Act provide the primary framework for regulations which control potential environmental impacts associated with oil shale development. Uncertainty over environmental requirements has been raised by some developers as a constraint to oil shale development. This paper attempts to dispel that notion.

Results to date of EPA research programs conducted to characterize residuals from oil shale processes, to develop appropriate monitoring methodologies and to demonstrate mitigating pollution control practices are discussed.

INTRODUCTION

EPA has legislative mandates (Figure 1) to protect air and water quality, to insure a safe drinking water supply, and to provide for an environment conducive for the enjoyment of man on this earth. In order to accomplish these goals, EPA is involved in a partnership with state and local environmental agencies (Figure 2) in the planning, implementation and enforcement of legislation and regulations. EPA and the State environmental agencies recognize that environmental considerations play a role in the determination of answers to the question of oil shale. How much? When?

This paper will (1) highlight the existing EPA environmental regulatory requirements for the oil shale industry, (2) describe EPA research directed toward answering the most important oil shale environmental questions facing regulators of the oil shale industry, (3) discuss the interrelationship between the regulatory and research effort, (4) discuss the relationships which EPA has attempted to develop with other agencies, with the industry and with the public in both the research and regulatory areas, (5) provide results, answers, and updates on progress and activities of EPA during the past year, (6) list outstanding environmental issues which need to be answered prior to the development of an oil shale industry, and (7) conclude with a discussion of the EPA Region VIII (and to a certain degree Agency) position on the way oil shale development could and should proceed.

REGULATORY ACTIVITIES

EPA is responsible for various regulatory activities which affect the construction and operation of oil shale facilities. Enabling legislation and implementing regulations in the form of the Clean Air Act Amendments of 1977 (P.L. 95-95), the Clean Water Act Amendments of 1977 (P.L. 95-217), the Safe Drinking Water Act of 1974 (P.L. 93-523), the Resource Conservation and Recovery Act of 1976 (P.L. 94-580), the Toxic Substances Control Act of 1976 (P.L. 94-469), and to a lesser extent the Noise Control Act of 1972 (P.L. 92-574) and the Federal Insecticide, Fungicide, and Rodenticide Act of 1975 (P.L. 94-140) establish the regulatory framework through which EPA operates. Of course, the National Environmental Policy Act of 1969, (P.L. 91-190) is also a significant piece of environmental legislation.

Under the Clean Air Act oil shale developers must (1) employ Best Available Control Technology (BACT), (2) insure that National Ambient Air Quality Standards (NAAQS) are not violated, (3) not cause Prevention of Significant Deterioration (PSD) ambient air quality increments to be violated, (4) not significantly degrade visibility in Class I areas and (5) perhaps obtain one year of baseline data prior to applying for a PSD permit to construct and operate. Region VIII has issued PSD permits for two developers (C-a and C-b), has proposed a permit for a commercial scale facility (Colony), and has received applications and/or letters requesting applicability determinations from seven other developers (Union, Paraho, TOSCO, Equity, Geokinetics, Occidental and DOE). BACT has been defined in the form of allowable emissions limits and control device operational characteristics.

The Clean Water Act contains requirements in Sections 301 and 404 for potential permits for an oil shale developer. A (NPDES) permit must be obtained under requirements of Section 402 if water is discharged to a navigable stream. A timetable for meeting the BPT and BAT effluent limitations was defined in the Clean Water Act by Congress (Figure 3). Specific effluent guidelines have not been promulgated for oil shale facilities. NPDES limits on core drilling, pump test activities and the initial retorting phase have been established by the state and EPA. A Section 404 permit must be issued by the Army Corps of Engineers and concurred upon by EPA if any dredge and fill operations take place in a navigable stream.

Underground injection control (UIC) regulations to be promulgated under the Safe Drinking Water Act govern the injection or reinjection of any fluids. Permits will probably be required for in situ operations and for mine dewatering reinjection. The State of Colorado requires reinjection permits under existing regulations. Monitoring and mitigation measures to prevent the endangerment of the groundwater system will be requirements under these UIC regulations.

The Resource Conservation and Recovery Act (RCRA) will govern the disposal of solid wastes generated by an oil shale facility. Criteria for the identification of hazardous wastes were proposed by EPA in December 1978. Performance standards and monitoring requirements for hazardous wastes were also proposed. Permits requiring safe disposal of hazardous wastes will have to be obtained from EPA or a state by an oil shale developer. EPA is presently evaluating how oil shale process wastes should be categorized within the hazardous/solid waste system.

Testing of effects, recordkeeping, reporting, and conditions for the manufacture and handling of toxic substances will be defined for oil shale developers under the auspices of the Toxic Substances Control Act of 1976. An inventory of all commercially produced chemical compounds has been compiled and is expected to be published by June 1979. Shale oil and its refined products are expected to be grandfathered under this system.

RESEARCH PROGRAM

EPA's energy research program must be responsive to Program Office and Regional Office regulatory needs. Increased emphasis upon oil shale research activities within EPA occurred in the 1974-75 period with the concurrent occurrence of several factors including (1) the organization of the EPA Office of Energy, Minerals and Industry (OEMI); (2) the effects of the Arab Embargo and the launching of the Federal Prototype Oil Shale Leasing Program; and (3) the implementation of a congressionally mandated $100 million per year Interagency Energy/Environment Program. OEMI implements and coordinates EPA's energy related environmental/industry research and development efforts and also serves as the overall manager of the comprehensive Interagency Energy/Environment Research and Development Program. This program has established a mechanism to plan, coordinate, and fund research and development for clean energy use and pollution control technology activities within the 17 participating governmental agencies. Since the states in EPA's Region VIII contain major energy resources, including oil shale, the Region VIII Office works very closely with OEMI to plan and utilize the results from the R&D Energy Program.

The Research Program has been organized into five major categories. Figures 4 and 5 list for 1978 fiscal year, budgets for Energy-Related Processes and Effects, Processing, Overall Assessments, Extraction and Handling, and End Use. The energy-related processes and effects category has four significant subdivisions: health effects, ecological effects, measurement and monitoring, and environmental transport studies.

The total budget in support of the EPA Oil Shale Program in Fiscal Year (FY) 78 was $3.76 million as compared to $3.14 million in FY 77. Although the funding by category for FY 1979 is presently not available, the magnitude of the effort is currently only slightly larger than for FY 1978. An influx of funds into the program could be expected, however, if the commercialization of our nation's oil shale reserves is given primary importance in the National Energy Plan-II. The agencies participating in this program include: the Department of Energy, U.S. Geological Survey, National Bureau of Standards, U.S. Department of Agriculture, the Department of Navy, and the National Institute of Environmental Health Sciences.

Within EPA, 10 separate laboratories conduct or contract oil shale-related environmental studies. The Office of Energy, Minerals and Industry, Headquarters, acts as coordinator for the Interagency Program, but also contracted work in the area of overall assessments. OEMI's Industrial and Environmental Research Laboratory in Cincinnati (IERL-Ci) funds and manages research on processing, overall assessments, and extraction and handling. Research laboratories in Ada, Oklahoma; Athens, Georgia; Duluth, Minnesota; Las Vegas, Nevada; and Research Triangle Park, North Carolina conduct research studies in the processes and effects area. Shale oil product (end use) studies are managed and funded by both OEMI's Industrial Environmental Research Laboratory at Research Triangle Park (IERL-RTP) and the Ann Arbor (Michigan) Emission Control Technology Division (ECTD) of the Office of Air, Noise and Radiation.

Specific objectives of the EPA Oil Shale Program are two-fold: (1) the program is to support the regulatory goals of the Agency (Figure 6); (2) the research is to be directed towards ensuring that any oil shale industry to be developed will be accomplished in the most environmentally acceptable manner that is reasonably possible. To these ends, EPA is continuing to assess the research needs and environmental concerns expressed by the Department of Energy (DOE) and the oil shale industry.

Research is especially being directed to find solutions for the environmental problems expressed by the Department's Laramie Energy Technology Center, and the active developers. The Office of Research and Development/EPA is focusing on those efforts identified by the Laramie Center, since Laramie has a key role within DOE for managing and developing the technology of oil shale development.

OEMI is also providing the lead in the development of various oil shale/environment documents and reports such as the "Oil Shale and the Environment," "Oil Shale Research Overview," "Who's Who in Oil Shale," "Program Status Report: Oil Shale," and "Pollution Control Guidance for Oil Shale Development." OEMI has also formalized the interaction with industry in the form of a forum for the purpose of transferring results of EPA-sponsored research to industry and to catalyze cooperative research in mutual areas of environmental interest.

In 1974, in order to insure that there is internal coordination within EPA on oil shale research activities and needs, an intraagency Oil Shale Work Group was formed consisting of those EPA research staff who were engaged in the performance of oil shale research. The Regional Office is represented in order to provide researchers with information on development activities, liaison with developers, and regional regulatory needs.

Let me turn your attention to some of EPA's ongoing research activities. IERL-Ci has been studying the extraction and handling of raw shale and disposal of spent shale waste. Studies are underway to determine surface stability, water movement, water quality and revegetation of spent oil shale; to assess the environmental impact of leachates from raw mined oil shale; to define the nature, quantity, and composition of fugitive dust from mining, hauling, crushing, and transfer activities, to quantify the trace element composition of two cores from the Naval Oil Shale Reserve; and to assess the air emissions from oil oil shale operations and waste sites. Results to date on spent shale revegetation indicate that it can successfully be revegetated with the use of nitrogen and phosphorous fertilization, and irrigation, coupled with intensive management. Soil cover may be necessary in some cases. It has also been learned that boron and molybdenum accumulate in tissues of plants grown on spent shale.

IERL-Ci is also addressing retorting environmental concerns and pollution control technology. Research has been conducted in the areas of pollutant characterization, environmental analytical methods development, assessment of wastewater treatment and control technology, air pollution control for oil shale retorting, and overview of environmental problems. Plans call for the construction and field testing of portable pilot scale modules for air and water treatment methods to be tested on process streams.

EMSL-Las Vegas is managing an effort to design and implement an optimum groundwater monitoring network. As a first step in this effort, a compendium of reports on processes and process effluents had been completed. A second document addresses factors to be considered in the design of a groundwater monitoring network. Efforts to date have been completed in the Unitah Basin and work is progressing for a monitoring design for the modified in situ process in the Piceance Basin. EMSL-LV has also performed field efforts in the White River drainage of Utah and Colorado designed to define optimum surface water physical, chemical, and biological monitoring methods.

The ERL-Athens oil shale effort is aimed at characterization of retort effluent waters and the development of instruments and methods to characterize energy related wastes. Characterization of organic and inorganic compositions of potential wastewaters and of spent shale leachates is in progress.

The ERL-Ada program attempts to relate chemical changes in groundwater to the characteristics of the native rock and to changes that occur due to mining and retorting. By studying the transport process it is hoped that environmental impacts can be predicted more accurately.

Biological and health effects are being studied by ERL-Duluth, HERL-RTP, and ERL-Gulf Breeze. The ERL-Duluth program is providing baseline information on the aquatic environment existing prior to oil shale development and is also performing bioassays on retort process waters from the Paraho operation at Anvil Points. ERL-Gulf Breeze is studying the constituents of petroleum hydrocarbons which may accumulate in the marine food chain which may eventually be consumed by man. The HERL-RTP oil shale research program consists of a multitude of effects studies. Carcinogenic, mutagenic, and teratogenic studies of shale oil derived products, byproducts and wastes are being performed in both in vivo and in vitro laboratory experiments.

Air and water quality assurance programs are funded and managed by EMSL-RTP and EMSL-Ci, respectively. EPA research staff also manage the oil shale efforts performed by other Federal agencies involved in the interagency energy/environment program. Finally, oil shale development is one of the resources which was subjected to a Technology Assessment of Western Energy Resource Development which is being sponsored by OEMI.

In response to many requests from oil shale developers, DOE, the states, and the public, EPA is preparing a document entitled "Pollution Control Guidance for Oil Shale Development." This document attempts to capsulize the potential environmental impacts of an oil shale facility/industry. It also attempts to crystal ball the levels of pollution control which may be required of oil shale developers. This joint effort among researchers, program office staff, and regional office staff is an example of how the EPA oil shale program is tied together.

ANSWERS/UPDATES

I would next like to address several issues which have either been consistently discussed or have been raised in the past by the oil shale industry, other agencies and the public. This discussion will hopefully insure that we are all thinking on the same wavelength.

First, the number of permits required for a facility is consistently raised as a constraint. EPA is investigating opportunities for permit consolidation but I must ask the obvious question--How many of these permits are environmentally related? I might add that we have compiled a list of these permits and find that of the total number of permits and approvals, 15 are Federal. Second, the high background air quality levels of particulate, hydrocarbon, and ozone have been considered and discussed at length. EPA has responded in the form of development of rural fugitive dust policy, consideration of revocation of the hydrocarbon standard, revision of the ozone standard and the acknowledgement of the need for special consideration of high background rural ozone concentrations. Third, it has been argued that the inclusion of fugitive dust from oil shale activities is not consistent with the intent of PSD. The promulgated PSD regulations do not require consideration of fugitive dust emissions in evaluating compliance with PSD increments. Fourth, concern has been raised over the level of the proposed NSPS for electric utility facilities combusting oil shale derived products. It must be made perfectly clear that these standards will apply only to those facilities which sell more than one-third of their produced electricity and have a unit capacity of greater than 250 million Btu per hour. SO_2 emissions will be limited to a floor of 0.2 to a ceiling of 1.2 pounds per million Btu coupled with an 85 percent reduction. An option of an 80 percent reduction is being considered for use of synthetic fuels. The particulate limit will be set at 0.03 pounds per million Btu coupled with a 99 percent reduction. However, the percent reduction does not apply to liquid or gaseous fuels. The NO_x limit for synthetic oils or gas will be 0.5 pounds per million Btu. Conventional oil and gas limits are 0.3 and 0.2 respectively. Emission rates may be averaged over a 24-hour period. Further, I should add that one of the oil shale developer's PSD applications would indicate compliance with the gas-fired NSPS.

A fifth issue involves the Resource Conservation and Recovery Act. EPA is evaluating how high volume wastes should be addressed based upon comments received from the oil shale industry at the EPA public hearings. A sixth issue involves the PSD Class I/Class II designations and the necessity for redesignation. It is EPA's feeling the the development of a well controlled, environmentally sound facility should be able to exist within the constraints of a Class II designation. If Class III is needed it should not be needed until the oil shale industry becomes very mature.

Finally, uncertainties in the regulatory framework have been discussed. I would acknowledge that there are instances to support these statements. However, it is EPA's firm belief that environmental requirements are not a show-stopper for small modules or even the first couple of commercial facilities.

UNANSWERED ENVIRONMENTAL ISSUES

Mining and conversion of oil shale will degrade air quality, will consume precious water resources, may degrade surface and/or groundwater quality, will create solid and hazardous wastes to be disposed of properly, and will create significant population growth in a predominantly rural setting which translates into potential social and economic problems. That these things will occur is a given . . . the question is the magnitude and the significance of the occurrence. Key questions such as the following exist.

1. How much groundwater will be intercepted during mining?
2. What will the quality of potential discharges be?
3. Can groundwater quality be protected during and after _in situ_ retorting?
4. Can processed shale be disposed of properly without degrading ground or surface water quality?
5. Will revegetation of processed shale be successful over the long term?
6. What are the concentrations of various sulfur species in retort offgas streams?
7. What will be the air quality and visibility impact on the Flat Tops Wilderness Area (nearest Class I area)?
8. What are the expected trace element concentrations in air, water, and solid waste residual streams?
9. Is the conventional pollution control technology directly applicable to oil shale residuals? Is it as effective?

10. What is the expected population growth associated with the development of an oil shale industry?

Answers to the above questions (and perhaps other questions not yet posed) will in part determine the ability of individual plants and of an oil shale industry to be compatible with the desired environment for oil shale country.

Answers to some of the above questions may be partially answered by theoretical research work and limited-scope field investigations in the absence of any oil shale facilities. Answers to the remaining questions will necessarily be developed through rigorous testing programs and data analyses performed on facilities representative of commercial size.

CONCLUSIONS

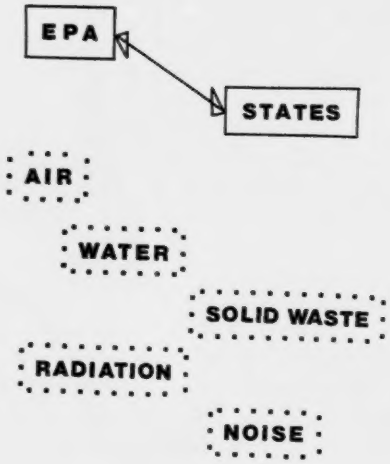
EPA recognizes that the development of the oil shale resources must play a role in satisfying the Nation's energy appetite. We are acutely cognizant of the need to accommodate national energy needs within a sound and reasonable environmental framework. We also recognize that there are uncertainties in air emissions, water quantity/quality information, solid waste characteristics, etc. EPA has and continues to acknowledge these uncertainties in the form of flexibility in permits granted to date. However, these uncertainties and unanswered questions coupled with our legislative mandates dictate that we take a position against the implementation of a large, e.g., 300,000 to 500,000 bpd industry until these uncertainties are resolved. An EPA preferred development option would be for the industry to construct and operate commercial-scale modules of different surface and *in situ* retort technologies as a first step. A second step would be the operation of a few (two or three) commercial facilities in order to answer remaining environmental questions and to assess cumulative impacts. Representative mining rates and methods should be evaluated. A maximum of 150,000 bpd should be developed and evaluated prior to Federal and state decisions being made which would allow or promote additional industry growth. A Prototype Leasing Program is a well designed program which should proceed to completion before additional leasing is proposed. EPA is not receptive to nor supportive of any plans or incentives which would encourage the rapid development of a large industry. There are too many environmental uncertainties associated with oil shale development to permit this magnitude of development.

FIGURE 1

EPA LEGISLATIVE MANDATES

CLEAN AIR ACT AMENDMENTS OF 1977	PL 95-95
CLEAN WATER ACT AMENDMENTS OF 1977	PL 95-217
SAFE DRINKING WATER ACT OF 1974	PL 93-523
RESOURCE CONSERVATION & RECOVERY ACT OF 1976	PL 94-580
TOXIC SUBSTANCES CONTROL ACT OF 1976	PL 94-469
NOISE CONTROL ACT OF 1972	PL 92-574
FEDERAL INSECTICIDE, FUNGICIDE, & RODENTICIDE ACT OF 1975	PL 94-140

FIGURE 2



EFFLUENT LIMITATIONS

JULY 1, 1977	BEST PRACTICABLE TECHNOLOGY
JULY 1, 1984	BEST AVAILABLE TECHNOLOGY FOR TOXIC POLLUTANTS BEST CONVENTIONAL TECHNOLOGY FOR POLLUTANTS SUCH AS BOD, TSS, PH, FECAL COLIFORM, & THERMAL
THREE YEARS AFTER PROMULGATION OF SPECIFIC EFFLUENT LIMITATION BUT NOT LATER THAN JULY 1, 1987	BEST AVAILABLE TECHNOLOGY FOR ALL OTHER IDENTIFIED POLLUTANTS

FIGURE 3

FY '78 OIL SHALE FUNDING SUMMARY

EPA/INTERAGENCY

ENERGY RELATED PROCESSES & EFFECTS	$ 1719 k
PROCESSING	1360
OVERALL ASSESSMENTS	331
EXTRACTION & HANDLING	280
END USE	65
TOTAL	$ 3755 k

FIGURE 4

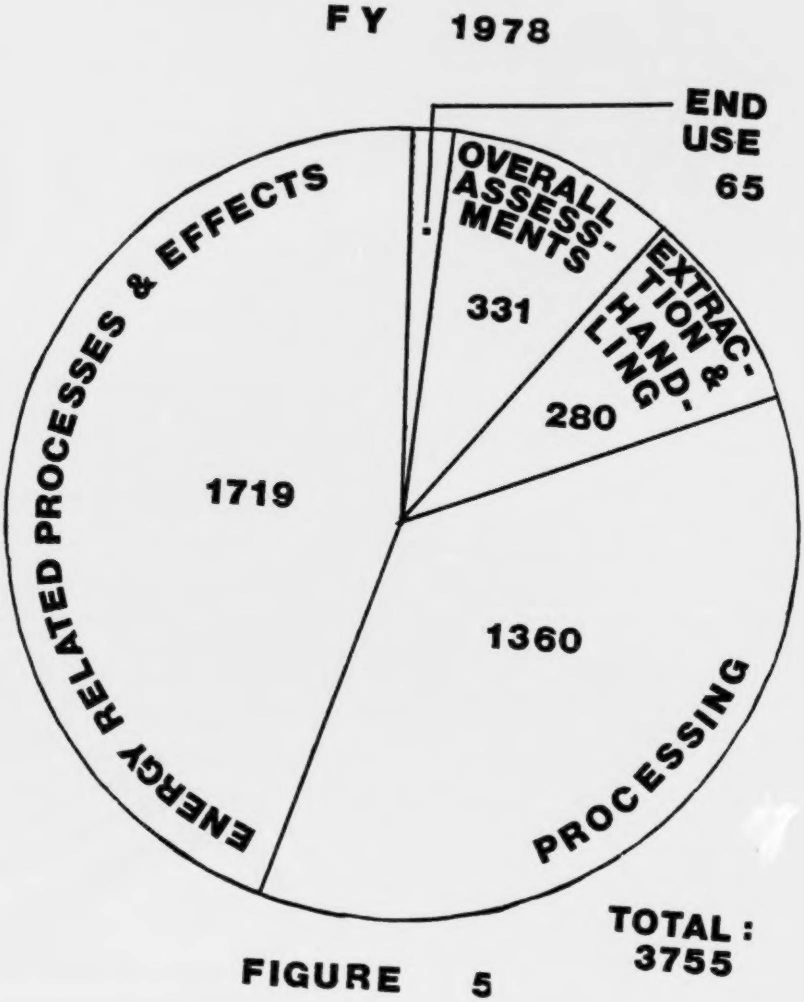


FIGURE 5

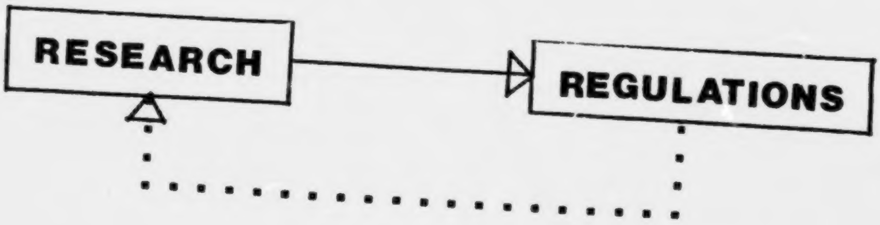


FIGURE 6

QUALITY ASSURANCE AS IMPOSED BY FEDERAL, STATE, AND LOCAL REGULATIONS

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This paper has two parts. The first part paints a bleak picture of oil shale quality assurance as imposed by Federal, state, and local government. Many or most of you undoubtedly have first-hand experience with the problems I will enumerate. The point of view in this assessment is that of a systems analyst charged with analyzing the total regulatory structure and reducing it to a system suitable for computer analysis.

The second part of the paper is more optimistic and timely. It describes efforts now underway to make the regulatory structure in the oil shale region more tractable, understandable, and efficient. All of us can contribute to this effort, and my paper concludes with an outline of the improvement program and its potential relationship to the oil shale community.

Since this is a gathering of scientists and engineers, one can infer that most of those present believe that the universe is one of law and order, and that man is capable of understanding this law and order. We all plan our lives to a large degree upon the assumption of this orderliness in nature, and we would like to plan our business activities upon an assumption that success is the predictable outcome of intelligent planning, creativity, and dedication.

It is strange that we cherish orderliness in nature, yet tolerate or even foster disorderliness in that which we jointly create: our culture. This paper attempts to demonstrate that all those concerned with oil shale are in danger of creating one of the most disorderly situations imaginable. If you will permit me to call something vitally important a game, then I can say that we may be structuring a game in which the greater one's planning, creativity, and dedication, the greater one's losses; the greater one's dedication to success, the greater one's risk of failure.

As an example, the call for papers to this symposium notes that the "U.S. Environmental Protection Agency has the responsibility to ensure that development of this (oil shale) resource proceeds in an environmentally acceptable manner." This statement has all the elements of orderliness. First, it lists a single agency, clothes that agency with sole responsibility for enforcement of a major rule of the game, and implies the objective or goal of the game. The agency, of course, is EPA, the implied objective is that "development of the oil shale resource proceed," and the rule which EPA is to enforce is that the players must stay within the environmental bounds. We note that development of the oil shale resource means that we need to make the transition from small-scale pilot programs, which are capable of yielding a limited amount of data, to a reasonably full-scale commercialization. We consider the benefits attainable through concerted efforts and healthy competition, and we conclude that there will be several teams, each hoping to score the most goals through intelligent planning, creativity, and dedication.

So far, so good. We have a goal, we have players, and we have a referee. Also, we know that there are supposed to be environmental bounds. But how are they set? Referring again to the call for papers to this symposium, we take somewhat out of context the statement that "Quality assurance (is) the critical review and acceptance of applicable methods and standards by a peer review system." This definition leaves room for us to talk about quality assurance as the rules of the game, and to infer that ideally these rules should be clearly established by our peers, that is, people who have equal standing with us in rank, quality, or accomplishment.

This definition of quality assurance, while much broader than alternative definitions concerned only with the reliability of monitoring data, is consistent with the role outlined for EPA, and will be used throughout this paper.

All of this can be summarized as shown in Figure 1. One can visualize that dedicated players participating in such a game would probably score some goals, providing the bounds were not made so narrow or irregular as to make the game physically impossible to play.

Unfortunately, as we start to examine how the game is really set up, we begin to wonder whether we've missed the real intent of the game. Our company, Science Applications, Inc., has been making a systems analysis of the oil shale regulatory system at the Federal, state, and county level. We've reached a midway point at which we can comment upon how the real game varies from the ideal game.

Figure 2 can serve as a point of departure for visualizing the regulatory system. This figure is an abstract of a 6 feet by 4 feet generic oil shale permitting chart developed during Phase I of our study. Each circle or node on the chart represents a permit, license, or approval involved in the life cycle of a typical oil shale project. Each diamond is a decision point which helps to establish the paths to be followed in a given case.

So far, we have referred only to EPA as the referee for our oil shale game. However, if one counts the number of cognizant or lead agencies for an oil shale development in Colorado, one finds that there are 56 referees in the generic case. These are mostly at the Federal and state level;

Figure 1

"IDEAL" OIL SHALE DEVELOPMENT

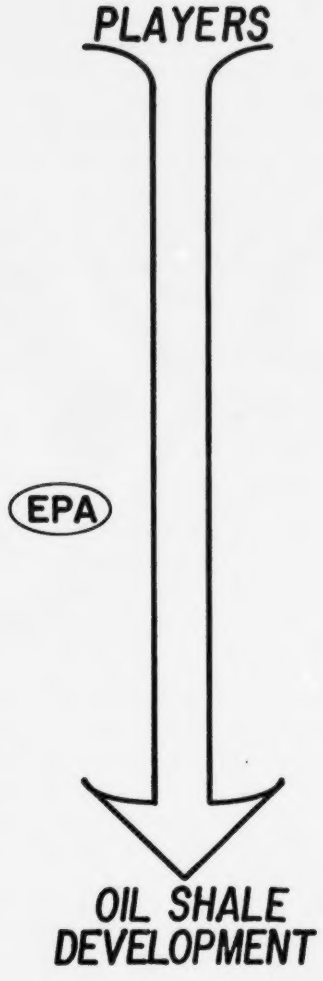
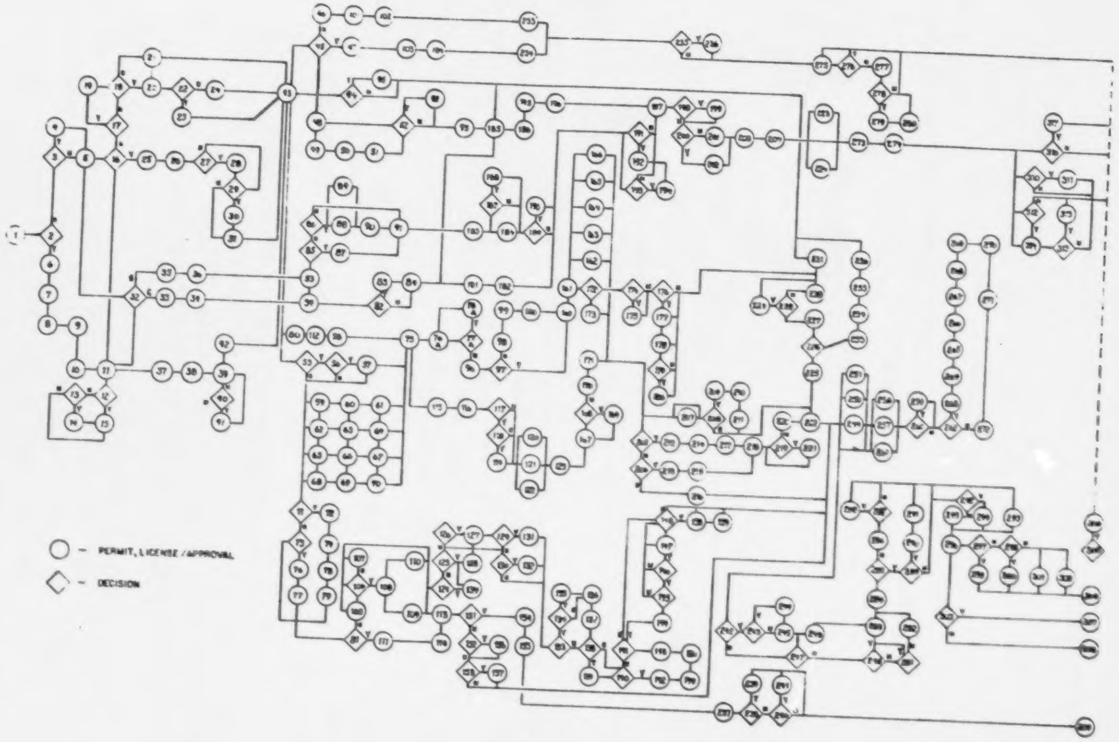


Figure 2

SIMPLIFIED REPRESENTATION OF GENERIC OIL SHALE PERMITTING PROCESS



because this is a generic flow chart, it is difficult to show the county referees in proper fashion.

This impressive array of referees does not line up together at the start of the game. EPA is highly visible, but some of the others are not. It is rather like a game in which new referees continually materialize as the contest proceeds.

The game is unusual in its treatment of fouls or penalties. In ordinary games, the officials confer in the case of suspected fouls, and in most games a team is allowed more than a single foul. One may be penalized on a disputable call by the referees, but the game is structured so that play can continue as long as the teams pay their penalties and give evidence of attempting to remain within bounds.

In contrast, in the regulatory game, anyone with a whistle can stop play indefinitely. The call may be controversial, and all the referees but one may wish the game to continue, but the oil shale game stops until the dissenting referee whistles the team back into play. It is difficult to say how many "sudden stoppers" there are in a complete oil shale game, but each cognizant agency has one or more.

Another significant feature of the oil shale game is its variability with time. We estimate that the entries in our oil shale data base will have a half-life of 10 years or less. A complete league game, by which I mean one which goes the full commercialization route, is likely to last beyond 10 years. Now, in most games, rule changes are imposed between games. Conversely, in our oil shale game a team may be sidelined as the result of decisions that were perfectly legal when they were made. The results of this type of game are likely to include continual revisions in strategy and a number of costly retrofits. Under such circumstances, it is possible that the team which pushes ahead most aggressively, without waiting for the dust to settle, will suffer the heaviest penalties. The contrast between this "new game" and the ideal game is shown in Figure 3.

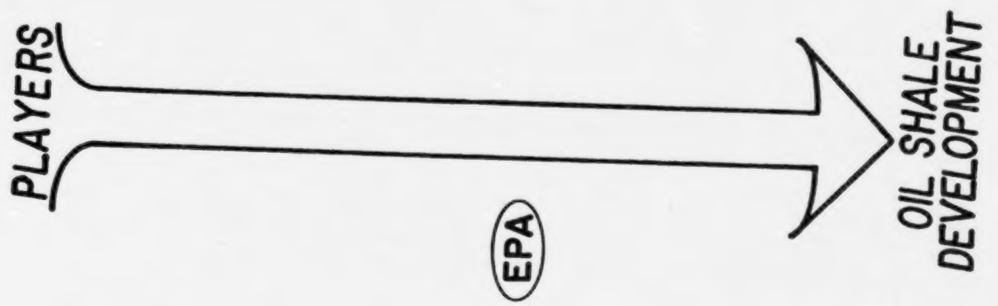
Another characteristic of successful games is that the referees are as inconspicuous and inobtrusive as possible. Their duties are well-defined. Where their authority or responsibilities overlap, they hold conferences as necessary and present a clear ruling to the players.

Again, these characteristics are not typical of the oil shale game. In our analysis, we classified permits by the type of environmental concern being protected, for example, air quality, water quality, or cultural values. Here, we reasoned that each government agency has one or more areas of responsibility and competence, and that redundancy of agencies should decline or disappear when classification of permits was introduced. However, this assumption proved false. Taking water quality as an example, we found that the 30 permits, licenses, and approvals in this path were administered by 14 separate agencies.

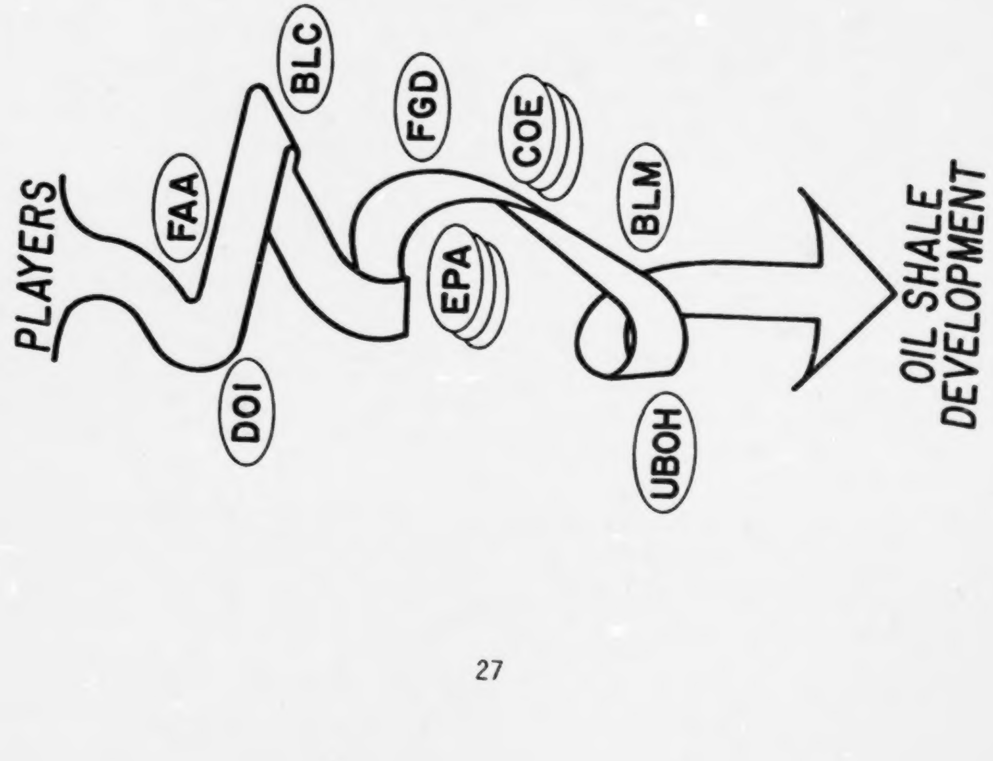
Figure 3

COMPARISON OF "IDEAL" AND "REAL" OIL SHALE DEVELOPMENT

"IDEAL" OIL SHALE DEVELOPMENT



"REAL" OIL SHALE DEVELOPMENT



This early in our study, we lack a reliable quantitative measure of redundancy in data requirements, but it is apparent that considerable redundancy exists. In some instances, the developer is required to repackage and resubmit the same basic information over and over again, as each referee in turn required evidence that the player is within bounds. This process has pitfalls for the player. He may design to a particular, known requirement or standard, and submit evidence of compliance, only to discover later that there is another, more stringent requirement imposed or administered by another agency.

Figure 4 summarizes the perceived problems in the existing regulatory system: a multiplicity of agencies involved in the process, requirements which increase with the passage of time, redundancies in data requirements, and variable interpretations of statutes and regulations. Many good reasons could be cited for each of the apparent defects in the system. However, from the standpoint of systems analysis, the net impact of the system is of primary concern. In this respect, the oil shale regulatory process reminds one of a question once posed by Dr. Samuel Johnson--

> "Consider, sir, how should you like, though conscious of your innocence, to be tried before a jury for a capital crime, once a week."

That approximates the net effect of a multitude of agencies, each with life-or-death authority over a given project, and with diverse and sometimes changing viewpoints regarding what is right and what is legal.

To summarize these findings, it would appear that a careful observer, perhaps newly deplaned or desaucered from Mars, might study the situation and decide that our oil shale regulatory game was cleverly designed to conceal its real purpose: while ostensibly designed to insure that development of our oil shale resource proceeds in an environmentally acceptable manner, its real intent is to ensure that development of our oil shale resource is postponed indefinitely. We, however, conclude that the men from Mars are wrong. The ostensible intent equals the real intent, but the game is so poorly defined that its real goal is in jeopardy.

How do we restructure the game? First, it seems clear that no single citizen or organization has the knowledge, skill, or authority to define or institute the needed changes. Oil shale development affects all levels of society, if only because we all use energy, buy from and sell to each other, and exist in a common physical environment. We have painstakingly set up a system of laws and a government of checks and balances, and this system has served us well. In such a society, we as professionals must avoid the traps of indolence and arrogance. We must attempt to raise the level of debate, and place it upon an objective plane. There is need for a concerted effort to do the following things.

1. State the options and objectives, in terms of what the development or abandonment of oil shale can mean to each representative group.

Figure 4

SUMMARY OF PERMITTING PROBLEMS

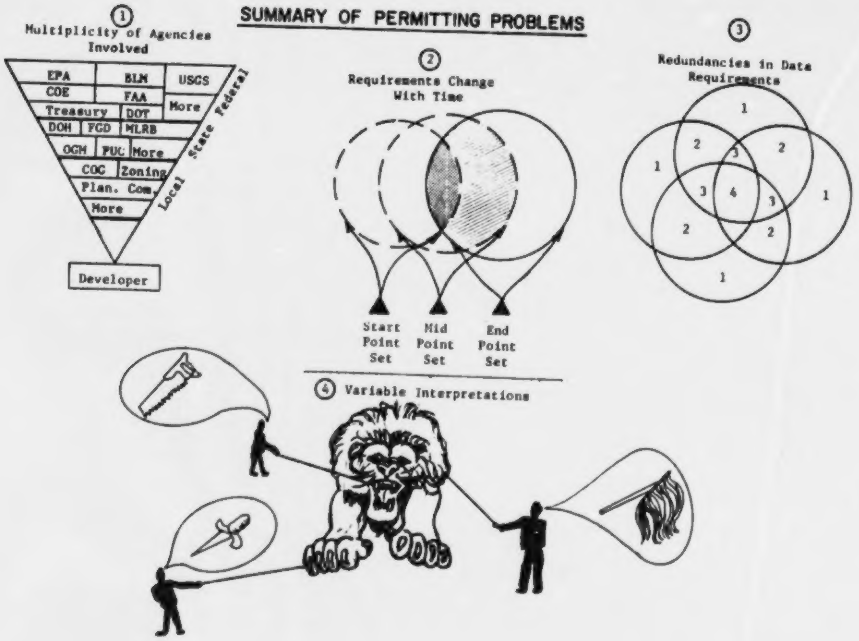
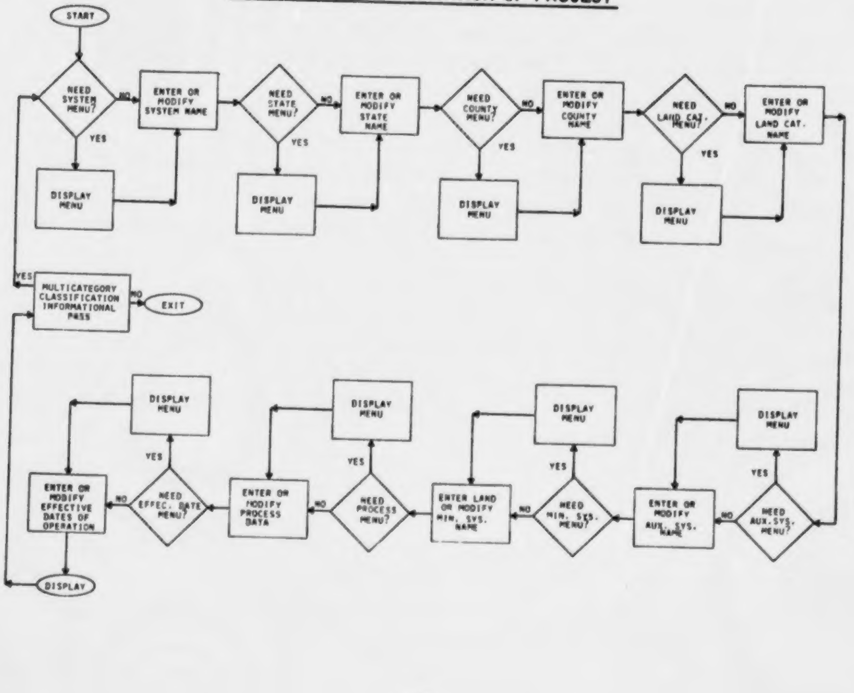


Figure 5

INTERACTIVE CLASSIFICATION OF PROJECT



2. Define the sense of the regulatory system, including classification of all system elements as complementary, redundant, or conflicting.

3. Define the likely impact of each element of the regulatory system upon the energy objectives and the sense of the regulatory system.

4. Design a spectrum of improved regulatory systems, ranging from one which fulfilled all senses of the regulatory system at minimum cost to the oil shale objectives to one which complied with all objectives of the oil shale development with minimum adverse impact upon the oil shale environment.

The Department of Energy, with the cooperation of many other organizations, is sponsoring the development of an automated information system which could facilitate these tasks. This information system, known as PERMISSO, will contain a data base of information on all permits, licenses, and approvals considered to be relevant to oil shale development in Colorado, Utah, and Wyoming.

PERMISSO will be an interactive or conversational system, with online response to requests for information. Figure 5 illustrates the interactive development of the typical input scenario. The system leads the user through a sequence which identifies the parameters which define the permit subset. The user can specify more than one scenario, and he can also specify the level of output data.

At the highest output level, the user obtains summaries of the number of agencies involved at each stage of the development, operation, and post-operation process, together with the nominal or average time requirements associated with each stage of the permitting process. At the next level, he obtains time-phased flow diagrams relevant to his operation. At the detailed level, he finds summaries of each permit or approval considered pertinent to his scenario, plus detailed lists of the technical data requirements imposed by the regulatory system. The existence of PERMISSO will make it relatively easy to discover redundancies and inconsistencies in the regulatory process, and to predict the impact of potential changes in the system.

Many people in government and industry have contributed information needed for the design of the system. The States of Colorado, Utah, and Wyoming have expressed their desire to improve the regulatory structure in their areas, and plans for using PERMISSO as a tool in a comprehensive review process are being formulated. Federal and local agencies are expected to participate in these activities.

Thus, there is a widespread desire to improve the imposed quality control structure, and tools are being developed to facilitate such improvement. My hope is that all members of the oil shale community will be equipped to make a vital contribution to the decision process as it relates to energy and the environment. Our analyses suggest that each developer's quality assurance program must be consistent with the total regulatory structure, and that the regulatory structure must be optimized with respect to human needs. Current world events suggest that we can no longer afford the luxuries of confusion and inefficiency in our control of energy development.

SAMPLING DESIGN FOR BASELINE STUDIES OF THE COLORADO OIL SHALE REGION

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ABSTRACT

Sampling of large volumes of heterogeneous material for trace element studies requires considerable care in sample design. The trace element baseline studies of the oil shale region are used as an example of the problems encountered in sampling soils, stream sediments, and plants over relatively large areas.

Hierarchial or nested analysis of variance is being used in sampling surficial materials in the Colorado portion of the oil shale area. This technique permits sampling in an economical way that will reveal trends in the baseline, if present, that are not an artifact of the sampling. Natural materials such as soils and stream sediments (in an area of horizontal sedimentary rocks) tend to be relatively heterogeneous on a small-scale, but can be homogeneous on a large-scale. The analysis of variance technique allows the determination of the geographic scale where the bulk of the natural variance occurs. This in turn permits sampling at an interval that makes efficient baselines. The elements of most concern are those which are geochemically mobile under the alkaline conditions found in the oil shale region or volatile under the reducing conditions of retorting.

In the initial study of soils over the Piceance Creek Basin, natural, large-scale trends were found for Zn, Li, Fe, Cu, B, Ca, Mg, and a few other elements of lesser importance. Stream sediments exhibit significant variation between drainages and at an extremely small-scale.

Intermediate scale analysis of variance studies and grid studies were done on areas surrounding oil shale Tracts C-a and C-b. Detectable geochemical trends were observed for Li, Mo, B, As, and organic carbon in soils and Mo in Big sage on tract C-a and vicinity. The natural trends are due to subtle geologic variations and would be expected based upon outcrops of the uppermost portion of the Parachute Creek member in the western part of the area. Tract C-b is entirely on the overlying Uinta formation and natural trends in the area are weaker or nonexistent. Weak trends exist for Li and pH in soil and for B and Mo in Big sage.

INTRODUCTION

The error in monitoring or determining the composition of a natural system can be divided into several components. In the simplest cases these might be, sampling location and sampling procedure error, measurement or analytical error, interpretative and manipulative error. Most attention is generally directed toward the measurement systems and their accuracy and precision. This work will be devoted to the sampling problems.

Study of physically large systems, heterogeneous systems, or systems that exhibit considerable variation with time present special sampling problems. In general, sampling and sampling location errors can be expected to be larger than the other contributions to total error in systems of this type. Frequently, the least amount of effort is devoted to reducing this component of the error.

The chemistry of surface soils, plants, and stream sediments of the Colorado oil shale region are being studied to establish baseline concentrations. This is a case of quantifying the composition of several physically large systems of unknown homogeneity. For the top 1cm of soil this is a target population of approximately 10^{14}g spread over 5,000 sq km. The description of this material must be in a manner that represents an efficient use of field and laboratory resources.

For purposes of this study, a baseline is defined to be a reference that not only describes the mean and limits of concentration inherent in nature, but also quantifies the geographic scale of variability. An effective way of expressing this baseline is with a geochemical map. If the area is homogeneous this is an excellent means. If the variability is local, too many samples will be required to develop a stable or reproducible geochemical map. In this case, a mean and expected range is a more appropriate way of expressing the baseline. Constructing a contour map when the majority of the variance is at local geographic scales results in a map that appears satisfactory but is an artifact of the samples and may not be reproducible.

REGIONAL SOILS STUDY

The sampling design for the study of the soils in the Colorado oil shale area or Piceance Creek Basin is a partially unbalanced nested or hierarchial analysis of variance design described by Miesch of the U.S. Geological Survey.[1,2] The regional study was considered reconnaissance in nature, with objectives of ascertaining the general chemical character of the soils, regional trends if any, and developing guidelines for sampling design in more localized studies.[3] Figure 1 is a simplified geologic map of the area, showing the locations of Tracts C-a and C-b and the major drainages of the area.

The initial sampling design, as used in the field, was balanced. Within each of 36 townships (36 square miles each), two sections (1 square mile each) were chosen at random. Within each section, two samples of surface soil were collected 100 meters apart (Figure 2). The soil develop-

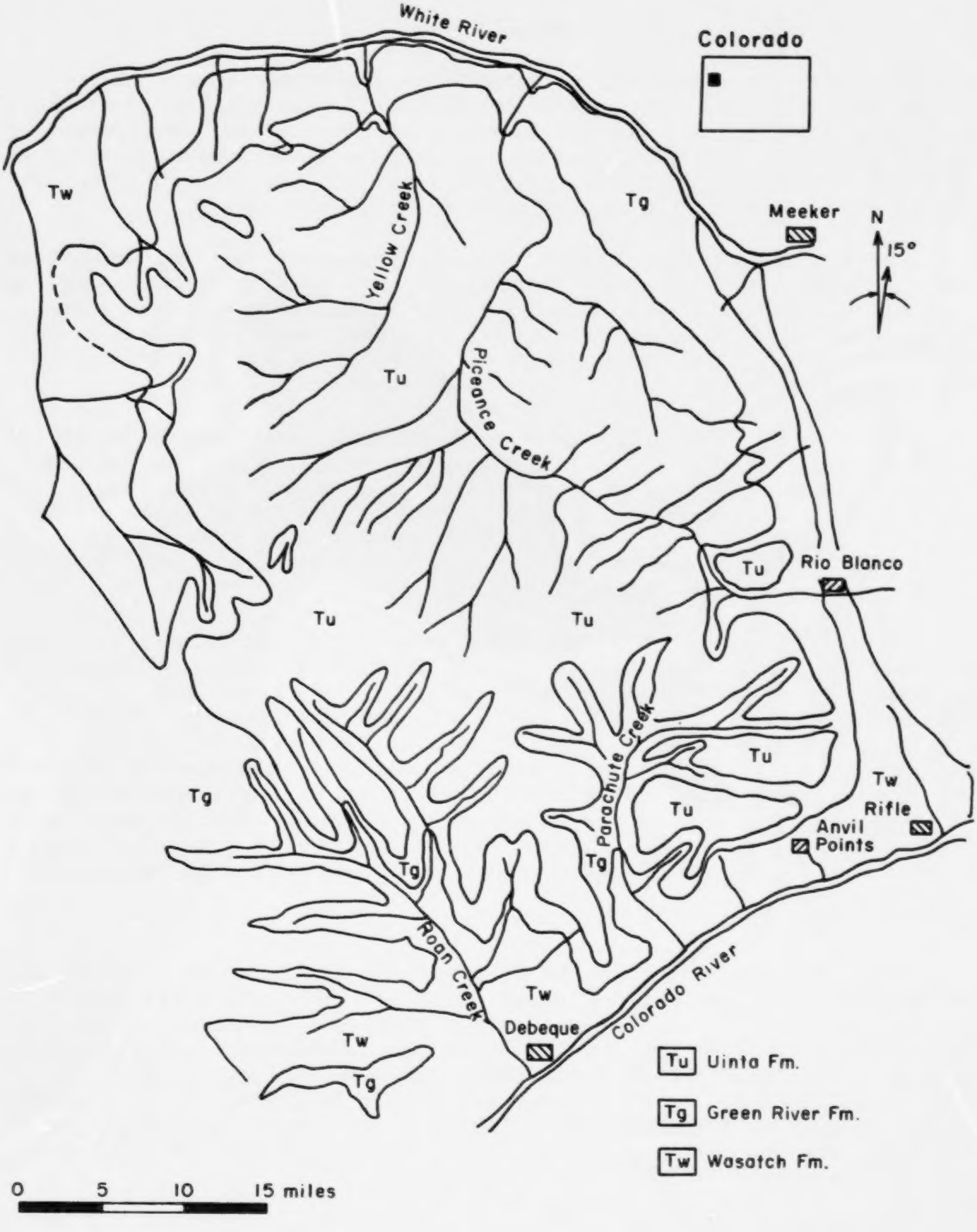

Figure 1. Simplified Geologic Map of the Colorado Portion of the Oil Shale Area.

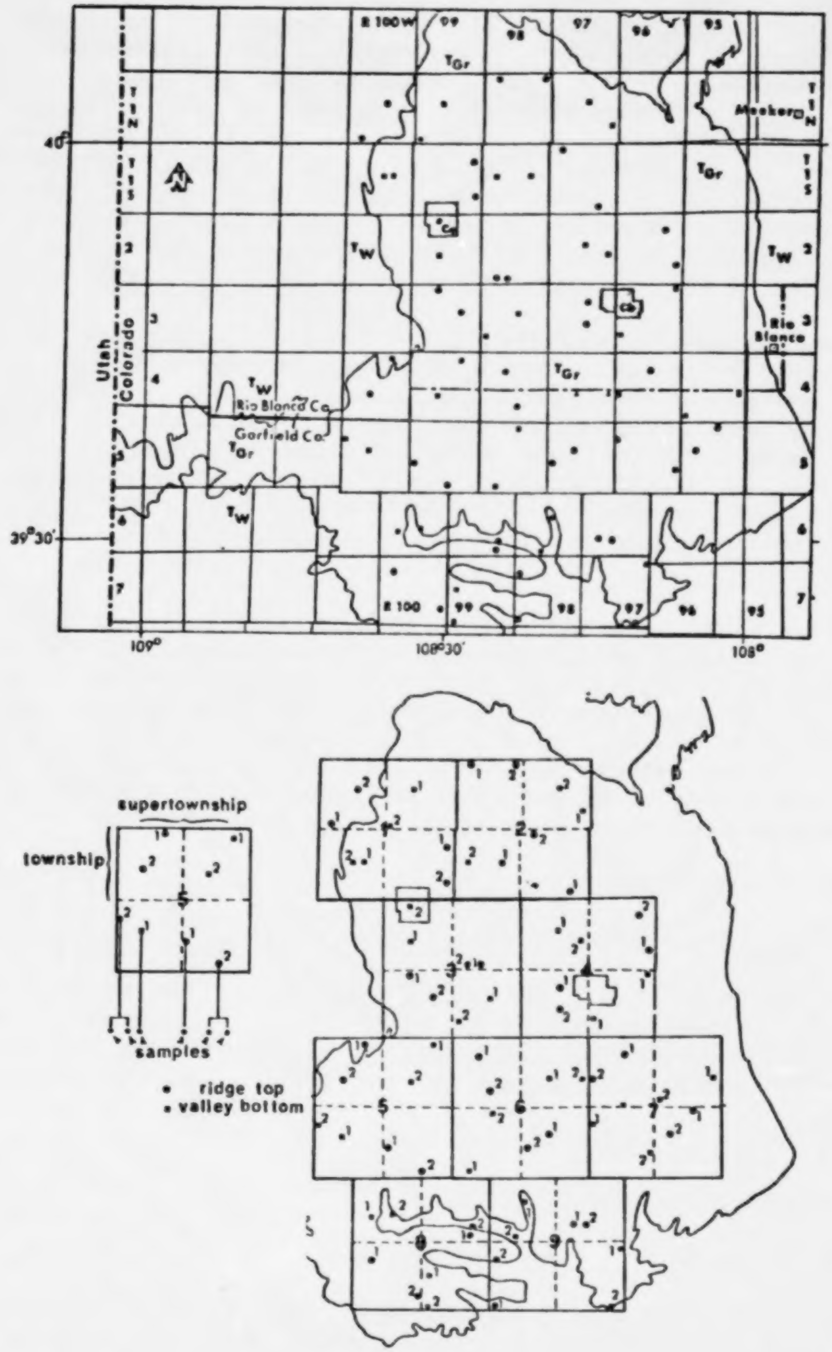

Figure 2. Index Map (top) Showing Location of Study Area, Lease Tracts C-a and C-b and Soil Sampling Localities. Map (bottom) Showing Soil Sampling Design and Number of Samples at Each Locality.

ment and plant ecosystem exhibit substantial physical differences between the relatively flat ridge tops and flat valley floors. It was expected that chemical differences might also be observed, so this feature was incorporated into the design. All four samples within a given township were collected either from ridge tops or valley bottoms. Ridge top and valley sampling alternated according to a checkerboard design. Four townships were grouped into "supertownships" (Figure 2). By randomly eliminating one sample from one section in each township, an unbalanced design at the sample level resulted in a reduction of analytical load by 25 percent. These samples were analyzed by the U.S. Geological Survey. Thirty-two randomly selected samples of the 108 used in this design were replicated in analysis.

Soil samples were a composite of the top 1 inch taken over an area at least 10-meters in radius. They were sieved through a 4 mesh stainless steel sieve and stored in stream sediment bags. Stream sediments from the regional study were collected at one location from a sand bar away from overhanging banks. In the more localized studies, stream sediments were composited over at least 10m of stream channel. All samples were field sieved to -4 mesh and stored in stream sediment bags. The samples were split to 12-15g and ground to -200 mesh in tungsten carbide for trace element analysis.

The final design consists of six levels. Level 1 is physiographic and will determine if there are geochemical differences between soils on ridge tops and those in valley bottoms; level 2 was designed to examine geochemical differences at geographic scales greater than 19km (between supertownships); level 3 at scales from 3 to 19km (between townships); level 4 at scales from 0.1-3km (between samples); level 5 at a scale of 100m (between samples); level 6 estimates analytical precision and includes errors due to sample inhomogeneity, sample preparation and analysis.

The model is defined as:

$$X_{ijklmn} = \mu + a_i + b_{ij} + c_{ijk} + d_{ijkl} + e_{ijklm} + f_{ijklmn} \qquad (1)$$

where μ is the mean of all the nested samples, a_i is the physiographic component, b_{ij} is the regional component (> 19km), c_{ijk} is the 3-19km component, d_{ijkl} is the 0.1-3km component, e_{ijklm} is the 100m component, and f_{ijklmn} is the analytical component. The total population variance is:

$$\sigma_x^2 + \sigma_a^2 + \sigma_b^2 + \sigma_c^2 + \sigma_d^2 + \sigma_e^2 + \sigma_f^2 \qquad (2)$$

and is calculated as the sample variance:

$$S_x^2 = S_a^2 + S_b^2 + S_c^2 + S_d^2 + S_e^2 + S_f^2 \qquad (3)$$

In the interpretation of the analysis of variance design, ratios of the variances at different levels of the sampling model are examined. The variance ratio (V) is the ratio of the variance among the localities to the variance within them. For example, the larger the variance ratio:

$$V = \frac{N_v}{D_v} = \frac{S_a^2}{S_b^2 + S_c^2 + S_d^2 + S_e^2 + S_f^2} \quad (4)$$

the more significant is the physiographic component of variance. The same procedure can be applied to the next component of variance in order to determine if there is a regional component of variance for any given element.

Table 1 summarizes the distribution of the variance among the six levels for each of 37 elements. It must be emphasized that this was a reconnaissance survey and many of the determinations were by semiquantitative optical emission spectrography. As a result, the analytical component of variance is large for many elements such as Sb. In this case, the only useful information is that the analytical technique is not adequate. Most of the geographic variance for most elements occurs between sections (0.1 to 3km). Of the 37 elements listed in Table 1, 27 have significant variance at the section level (Al, Ca, Fe, Mg, K, Si, Na, Ti, As, B, Ba, Be, Co, Cr, Cu, Ga, Hg, Li, Mo, Pb, Rb, Sc, Sr, V, Y, Yb, and Zn).

Only 10 elements (Al, K, Si, Na, Ti, F, Li, Ni, Zn and total C) have significant variance components at the sample level (100-meter distance) and only five elements (Ca, Na, Hg, Sr, and total C) have significant variance components at the township level (3-19km). More than one-third of the elements listed in Table 1 (14 of 37) have significant variability between supertownships (> 19km). These 14 elements include Ca, Fe, Mg, Si, Ti, B, Be, Cr, Cu, Ga, Li, Y, Yb, and Zn. Although soil development and characteristic vegetation on ridge tops visibly differ from that in valley bottoms, there were no significant elemental differences between soil samples collected on ridge tops and those collected in valley bottoms. This means that the ridge top and valley bottom samples can be viewed as part of the same population. It was expected that there would be differences between ridge tops and valley bottoms due to differences in soil development and vegetative cover.

By a quantitative examination of the distribution of the variance it can be determined that the sampling was adequate to describe the variability for five elements (Fe, Be, Cu, Li, and Zn) in a map form. If most of the variance is at the upper geographic scales, a relatively limited number of samples will produce a stable (reproducible) geochemical map. If the variance is concentrated at local scales as is the case for As, only small-scale sampling will allow a map representation of the As concentrations in soils. In this case, sampling and analytical costs restrict the description of the basinwide data to a mean, range, and deviation.

All five elements for which stable geochemical maps can be made show higher concentrations in the southern part of the basin and three (Cu, Li, and Zn) exhibit well-defined trends in that direction. Concentrations of soil Zn increase from 68ppm in the northeastern part of the basin to almost 100ppm in the southwestern part. Figure 3 illustrates the Zn distribution.

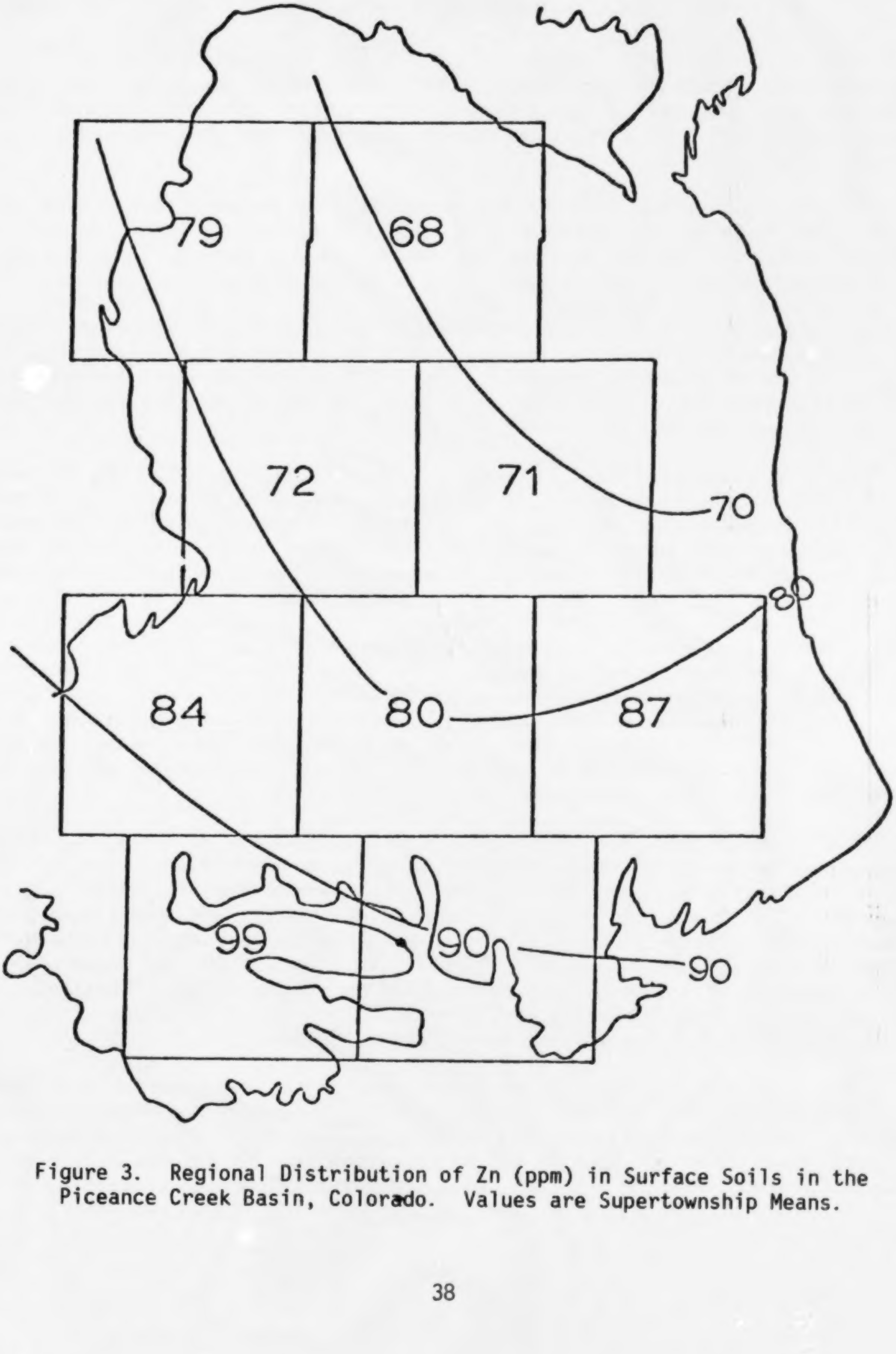

Figure 3. Regional Distribution of Zn (ppm) in Surface Soils in the Piceance Creek Basin, Colorado. Values are Supertownship Means.

TABLE 1. ANALYSIS OF VARIANCE OF SURFACE SOIL CHEMISTRY, PICEANCE CREEK BASIN, COLORADO

			Variance Components as Percentage of Total Variance				
Element	Total Logarithmic Variance	Between Ridge Tops and Valley Bottoms	Between Super-Townships (>19km)	Between Townships (3-19km)	Between Sections (0.1-3km)	Between Samples (0-100m)	Analytical Error
Al	0.0044	0	18	0	58*	14*	10
Ca	.1596	0	28*	15*	48*	9	0
Fe	.0080	0	27*	0	38*	2	33
Mg	.0291	0	28*	3	57*	1	11
K	.0075	2	7	0	80*	6*	5
Si	.0038	0	22*	0	46*	22*	10
Na	.0473	0	4	41*	46*	6*	3
Ti	.0064	1	28*	0	54*	9*	8
Total C	.0535	1	14	26*	19	31*	10
As	.0914	0	0	0	81*	6	13
B	.0173	0	18*	0	57*	5	21
Ba	.0313	0	0	0	35*	6	58
Be	.0264	0	24*	0	37*	0	39
Co	.0624	0	12	0	33*	0	55
Cr	.0452	0	17*	0	37*	0	46
Cu	.0821	0	28*	0	18*	1	52
F	.0331	3	7	0	15	34*	41
Ga	.0677	0	10*	0	59*	0	32
Ge	.1378	0	0	11	0	27	62
Hg	.1631	2	10	36*	31*	4	17
Li	.0363	5	23*	0	58*	10*	5
Mn	.0476	0	0	8	4	0	88
Mo	.0976	0	11	0	48*	7	33
Nb	.1055	0	1	0	17	0	82
Ni	.0694	0	10	0	24	36*	30
Pb	.1029	0	6	0	39*	0	55

TABLE 1. (CONT.)

Element	Total Logarithmic Variance	Between Ridge Tops and Valley Bottoms	Variance Components as Percentage of Total Variance				
			Between Super-Townships (>19km)	Between Townships (3-19km)	Between Sections (0,1-3km)	Between Samples (0-100m)	Analytical Error
Rb	.0127	0	6	0	77*	6	11
Sb	.1867	1	2	0	0	10	86
Sc	.0491	0	5	0	37*	0	59
Se	.0947	1	0	15	0	25	59
Sn	.3488	0	2	0	0	33	65
Sr	.0350	1	19	18*	31*	5	27
V	.0396	0	7	0	52*	0	41
Y	.0330	0	9*	0	42*	0	49
Yb	.0986	0	8*	0	38*	0	54
Zn	.0083	1	31*	12	32*	19*	5
Zr	.0359	2	1	0	28	2	66

A more detailed discussion of the results of the first phase soil studies is published.[3]

REGIONAL STREAM SEDIMENTS STUDY

As in the case of the regional soils study, the initial stream sediment studies were of a reconnaissance nature.[4] There were two components to the regional stream sediment study; one to determine if anomalous drainages of areas existed, and the other a hierarchial analysis of variance design to quantify geographic variability and enable planning of the more localized studies to follow. Only the analysis of variance portion of the work will be described here.

An estimate of the natural variability in five major drainages was determined using the hierarchial analysis of variance design of Miesch[1,2] but modified to fit a one-dimensional stream channel.[4] Figure 4 illustrates the various geographic scales in the stream channel sampling, which partition the variance in a 10km stream channel segment. Within each of these 2km segments, two 200 meter segments were picked at random, one within each 1km segment. Then each 100 meter segment. Finally within each 20m segment,

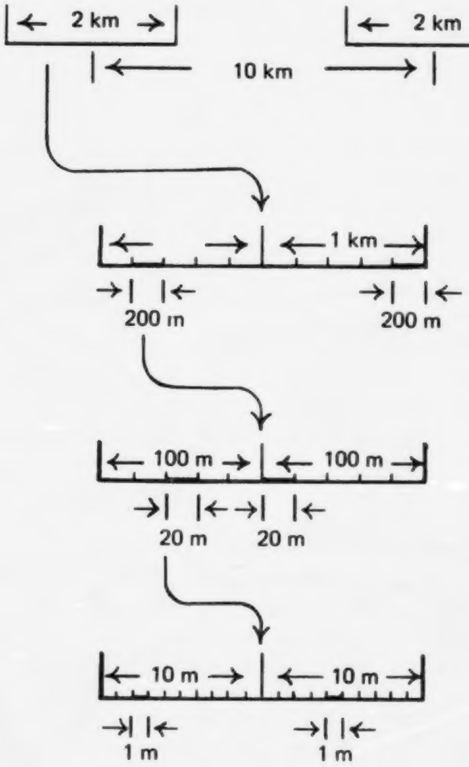

Figure 4. Details of Stream Sediment Analysis of Variance Sample Design.

two samples were collected over a distance of 1 meter, one within each 10m segment. The variance is partitioned in a manner analogous to equation (3), but with five components, all geographic scales.

One of the hierarchial stream sediment sampling models is randomly placed in each of the five major streams of the basin as shown in Figure 5. The dashed lines across the streams show the predefined limits of the main stem that will possibly be in the 10km segment to be sampled. The dashed boxes show the actual position of the randomly placed 10km hierarchial model in the individual stream drainages.

The streams in the Roan Plateau area (Piceance, Black Sulfur, Yellow Creeks) dissect the Uinta sandstone. The heads of these streams flowing easterly or westerly cut into the upper portion of the Parachute Creek member. This moderate dissection contrasts with the extreme dissection of a large stratigraphic interval by Roan Creek and Parachute Creek (Figures 1, 5).

The analysis of variance of the nested design for the major streams in the Piceance Basin is summarized in Table 2 for a few elements. From the table two variance components stand out: the variance from 0-10m for the individual streams, and the variance between streams for all stream data. The significance from 0-10m for Mo cannot be tested because the 0-10m scale of variance and the analytical variance are combined in the lowest level, but the high percentage of the variance at this lowest level is an indication that 0-10m would be significant if a test could be made. In general, the consistency of the significance at the 0-10m scale may be reflection of the power (degrees of freedom) of the sample design being concentrated at the lower levels. Except for Zn, there are significant differences between streams for all the constituents. A similar study done in the same area and in Utah also brought out the significant difference between streams for many other elements.[5] Semiquantitative optical spectrography data for B in sediments from Roan and Black Sulfur Creeks indicate an elevated concentration (geometric mean of 44ppm) with most of the variance concentrated at intermediate geographic scales. Summmary data published by McNeal and others[5] gives geometric means of 6.5 and 7.8ppm, respectively for As and F in stream sediments. The As is elevated in concentration with respect to the earth's crust but not with respect to an average scale. The F is substantially depleted, possibly due to solubility under the alkaline conditions of the basin.

In the analysis of variance component of the regional reconnaissance stream study a total of 80 samples were collected (16 from each of five streams). From this rather limited sampling we can obtain a number of relatively important pieces of information about stream sediments. A preliminary estimate of means, deviation, and ranges can be obtained through additional sampling and will improve the estimates. The most important information is that individual streams are geochemically different and there is a large component of variance in the 0-10m scale. This implies that in future sampling of stream sediments, all drainages should be sampled, they

TABLE 2. GEOCHEMICAL SUMMARIES FOR STREAM SEDIMENTS OF MAJOR CREEKS IN THE PICEANCE BASIN

(Data given in parts per million; an asterisk (*) indicates variance component is significantly different from zero at the 0.05 probability level)

			Analysis of Logarithmic Variance					
		Total	Percent of Total Variance					
Element	Stream	Log_{10} Variance	Between Streams	1-10 km	100m -1km	100m -10km	0-10m	Anal. Error**
Mo	All	.0052	73*	.2	0	3	17	6
	Roan	.0159	-	0	13	0	87	-
	Black Sul..	.0365	-	15	1	0	76	8
	Piceance	.0143	-	0	0	21	79	-
	Parachute	.0044	-	5	4	0	91	-
	Yellow	.0215	-	38	0	4	58	-
Zn	All	.0066	36	18	2	3*	33*	7
	Roan	.0134	-	27	10	0	47	17
	Black Sul.	.0030	-	46	3	10	37*	4
	Piceance	.0011	-	0	0	9	91*	0
	Parachute	.0012	-	14	0	37	40	9
	Yellow	.0036	-	30	0	9	48	14
Hg	All	.0614	66*	6*	0	0	20*	8
	Roan	.0162	-	8	6	0	80*	9
	Black Sul.	.0375	-	38	0	13	43*	6
	Piceance	.0214	-	11	0	23	54*	12
	Parachute	.0333	-	0	6	0	61*	33
	Yellow	.0085	-	1	0	26	0	73
Organic Carbon	All	.1831	69*	12*	3	0	16*	0
	Roan	.0835	-	20	6	4	71*	0
	Black Sul.	.1416	-	50	8	0	39*	0
	Piceance	.0198	-	60	10	0	30	-
	Parachute	.0011	-	17	43	12.4	22	5
	Yellow	.0326	-	1	22	0	76	1

**The analytical component is included in the 0-10m component where a-appears.

SUMMARY STATISTICS

Geometric Mean	Geometric Deviation	Geometric Error	Expected 95% Range
4.2	1.64	1.09	1.6-11.1
3.5	1.28	-	2.1-5.7
2.9	1.41	1.09	1.5-5.6
4.2	1.33	-	24.0-7.4
9.5	1.14	-	7.3-12.3
3.3	1.34	-	1.8-5.9
61.0	1.20	1.03	28.6-129.0
63.8	1.28	1.08	39.9-102.0
53.3	1.12	1.01	42.5-66.0
67.8	1.08	1.00	58.1-79.0
68.9	1.06	1.02	61.3-77.0
52.5	1.13	1.04	41.7-66.0
.29	1.67	1.12	.11-78.0
.58	1.27	1.07	.37-.92
.36	1.44	1.08	.18-.73
.23	1.35	1.09	.13-41.0
.28	1.39	1.19	.16-.49
.15	1.19	1.14	.12-.19
.19	2.47	1	.15-5.55
1.26	1.87	1	.36-4.41
.79	2.01	1	.20-3.19
1.02	1.30	-	.60-1.72
2.54	1.07	1	2.22-2.9
.24	1.46	1	.11-.51

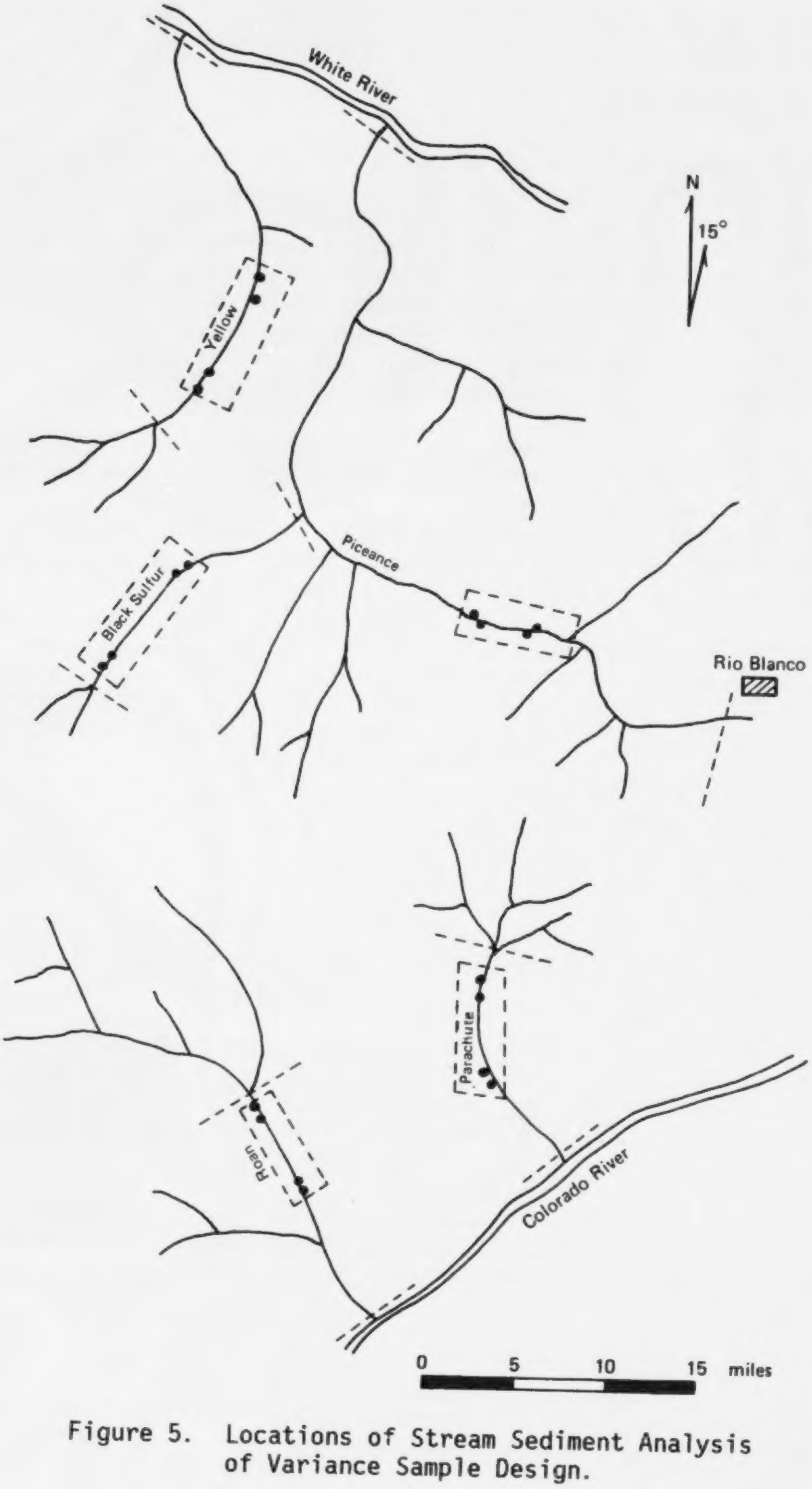

Figure 5. Locations of Stream Sediment Analysis of Variance Sample Design.

can be sampled at intermediate channel distances, and the individual samples should be a ocmposite of at least 10m of channel length.

TRACT C-a AND C-b STUDIES

The data from the regional soils study[3] and the regional stream sediment study[4] were used in planning the sampling for more localized studies. Plant materials were also added in the localized studies. Stream sediments were collected at the same time as soils and associated plants but generally have not been analyzed because of analytical capacity and remain for future studies. The results of the tract studies will be confined to soils and associated plants. The plant materials sampled included: Big sage (*Artemisia tridentata*), subspecies *tridentata* and *wyomingensis*, Indian ricegrass (*Oryzopsis hymenoides*) and Western wheatgrass (*Agropyron Smithii*).

Surface soil and plant samples were collected in a grid pattern over an area 8 miles by 6 miles, incorporating oil shale Tract C-a and over an area 9 miles by 5 miles, incorporating oil shale Tract C-b. The C-a study was the subject of a thesis by Candito[6] and C-b, a thesis by Zuccaro.[7] The grid sampling interval was 1/2 mile (0.8km) which was determined as an appropriate interval from the earlier study of Ringrose and others.[3]

A smaller-scale analysis of variance design was done in the local studies to confirm the results of the regional studies when applied to areas in the 40-50 sq mile range. The design consisted of randomly selecting four sections (1 sq mi) in the study area and collecting soils and plants analogous to Figure 6. The 1 square mile was quartered, two selected at random, quartered again, two selected at random, quartered a third time, and two sample sites collected 50m apart. The sample variance is distributed as:

$$S_x^2 = S_a^2 + S_b^2 + S_c^2 + S_d^2 + S_e^2 \qquad (5)$$

The levels are: variance at greater than 1.6km level, variance at the 0.4-1.6km level, 50m-0.4km level, variance between sample localities at the 50m level, and at the lowest level, analytical variance.

The trace element data exhibit a distribution that approaches lognormal as is generally the case for geochemical data. The data were log-transformed which changes the distribution to normal. Consequently, geometric means and deviations are calculated for the summary statistics (Tables 3, 4, 5, 6).

The geometric deviation calculated from log-transformed data can be adjusted for analytical error. This is particularly useful in estimating a concentration range for a material in a large area. The adjusted geometric deviation is calculated:

$$(GD)_n = [(GD)^2 - (GE)^2]^{\frac{1}{2}} \qquad (6)$$

where $(GD)_n$ is the normalized geometric deviation, GD is the geometric deviation and GE is the geometric deviation of the analytical replicates. A

95 percent expected range for the materials of the sampled area can be estimated according to Miesch:[1]

$$95\% \text{ Expected Range} = \frac{GM}{(GD)_n^{1.96}} \text{ to } GM \cdot (GD)_n^{1.96} \qquad (7)$$

The variance ratio (V, analogous to equation 4) is used to determine the significance of the regional component of variance. In the local context, the highest level is between sections (>1.6 km or 1 mi) to the sum of the variance at all lower levels. With the variance ratio, the effective number of random samples, N_r per square mile, required for a reasonable representation can be determined graphically.[1]

The maximum permissible error variance for a balanced design (E_r) is the ratio of the sum of all the variances except the highest level to N_r:

$$E_r = \frac{S_b^2 + S_c^2 + S_d^2 + S_e^2}{N_r} \qquad (8)$$

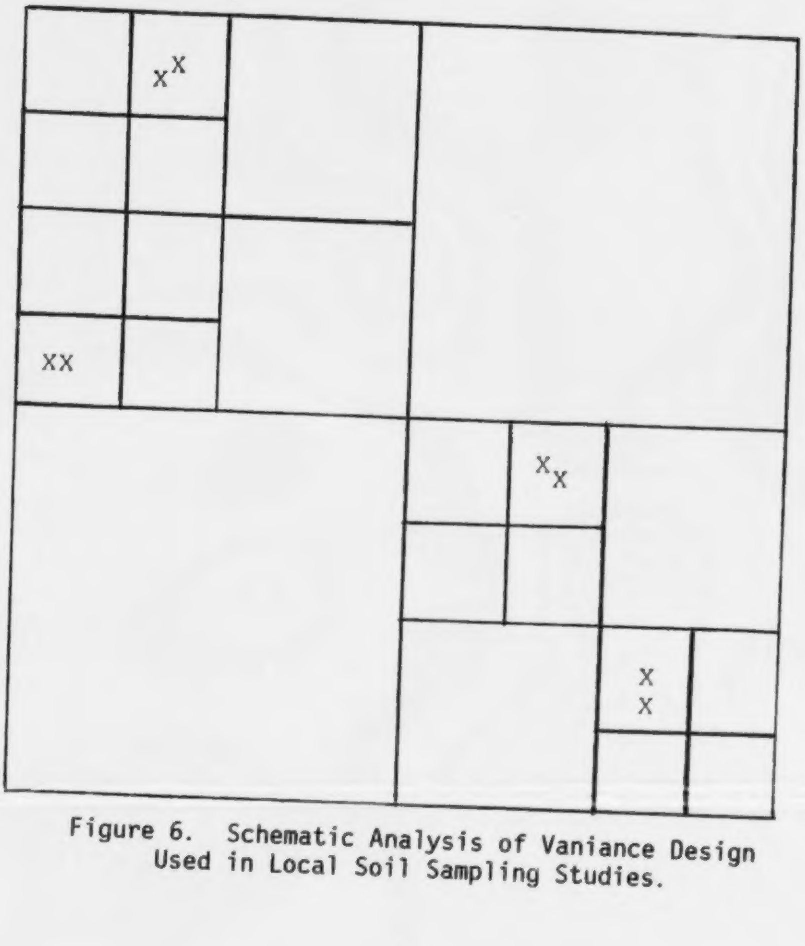

Figure 6. Schematic Analysis of Vaniance Design Used in Local Soil Sampling Studies.

TABLE 3. GEOMETRIC MEANS AND DEVIATIONS AND VARIANCE RESULTS FOR TRACE C-a AND VICINITY SOILS

Element	95% Expected Range	Geometric Mean*	Geometric Deviation*	Variance Ratio**	N_r	E_r	E_s	Number of Samples
Hg(ppb)	30.0-58.0	42.0	1.18	--	--	--	--	253.0
Zn(ppm)	39.0-123.0	70.0	1.33	0.02	45.0	0.019	0.0002	253.0
Li(ppm)	9.0-40.0	20.0	1.43	0.41	3.0	0.011	0.003	253.0
B (ppm)	78.0-195.0	123.0	1.26	--	--	--	--	253.0
Mo(ppm)	0.46-4.7	1.6	1.70	0.23	4.0	0.011	0.003	253.0
As(ppm)	4.0-18.0	8.7	1.43	1.36	2.0	0.0071	0.0048	32.0
Organic Carbon(%)	0.46-2.9	1.2	1.58	1.03	3.0	0.013	0.010	253.0
pH	7.1-8.5	7.8*	0.353*	--	--	--	--	253.0

*Arithmetic mean and standard deviation for pH (pH is a log measurement).

**If the estimated variance between sections is zero; N_r, E_r, E_s are not calculated.

TABLE 4. GEOMETRIC MEANS, DEVIATIONS, AND VARIANCE RESULTS FOR TRACT C-a AND VICINITY PLANT MATERIALS

	Element and Media	95% Expected Range	Geometric Mean	Geometric Deviation	Variance Ratio**	N_r	E_r	E_s	Number of Samples
Big sage	Zn(ppm)	0.43-11.0	2.2	2.26	0.02	45.0	0.004	0.001	32.0
	B (ppm)	21.5-42.6	30.3	1.19	0.46	2.0	0.0024	0.0006	249.0
	Mo(ppm)	0.25-1.7	0.65	1.63	0.22	5.0	0.0089	0.0026	243.0
Indian ricegrass	Hg(ppb)	11.0-52.0	24.0	1.47	0.05	60.0	0.00059	0.00061	32.0
	Zn(ppm)	0.49-18.0	2.6	2.46	--	--	--	--	32.0
	B (ppm)	3.0-32.0	10.0	1.81	0.02	45.0	0.0004	0.0001	32.0
	Mo(ppm)	0.48-2.3	1.1	1.48	0.24	4.0	0.0068	0.0017	32.0
Western wheatgrass	Hg(ppb)	7.5-70.0	23.0	1.75	--	--	--	--	25.0
	Zn(ppm)	5.1-18.0	9.6	1.38	--	--	--	--	25.0
	B (ppm)	7.7-28.0	15.0	1.38	--	--	--	--	25.0
	Mo(ppm)	0.54-2.4	1.2	1.45	--	--	--	--	25.0

**If the estimated variance between sections is zero; N_r, E_r, E_s are not calculated.

TABLE 5. GEOMETRIC MEANS, DEVIATIONS, AND VARIANCE RESULTS FOR TRACT C-b AND VICINITY SOILS

Element	95% Expected Range	Geometric Mean*	Geometric Deviation*	Variance Ratio**	N_r	E_e	E_s	Number of Samples
B (ppm)	73.0-208.0	136.0	1.28	0.0	--	--	--	40.0
F (ppm)	334.0-645.0	483.0	1.17	0.43	4.0	0.001	0.0004	58.0
Li(ppm)	21.4-26.2	23.8	1.20	0.54	3.0	0.001	0.0006	242.0
Hg(ppb)	16.8-26.3	21.5	2.39	0.0	--	--	--	243.0
Mo(ppm)	0.0-4.02	0.91	1.56	0.24	5.0	0.047	0.002	241.0
Zn(ppm)	63.1-67.7	65.4	1.16	0.42	3.0	0.001	0.0004	242.0
Organic Carbon(%)	0.0-6.73	1.52	2.60	0.40	4.0	0.020	0.008	243.0
pH	7.0-8.73	7.87	0.43	0.16	6.0	0.040	0.012	243.0

*Arithmetic mean and standard deviation for pH (pH is a log measurement).

**If the estimated variance between sections is zero; N_r, E_r, E_s are not calculated.

TABLE 6. GEOMETRIC MEANS, DEVIATIONS, AND VARIANCE RESULTS FOR TRACT C-b AND VICINITY PLANT MATERIALS

	Element and Media	95% Expected Range	Geometric Mean	Geometric Deviation	Variance Ratio	N_r	E_r	E_s	Number of Samples
Big sage	B (ppm)	24.7-29.6	27.1	1.22	0.13	7.0	0.001	0.0002	242.0
	Mo(ppm)	0.0-3.63	0.35	1.64	0.94	3.0	0.012	0.008	242.0
	F (ppm)	1.66-12.5	8.36	1.40	0.026	29.0	0.002	0.0003	36.0
Indian ricegrass	B (ppm)	2.13-17.7	9.18	1.49	1.53	2.0	0.007	0.005	57.0
	Mo(ppm)	0.03-2.16	0.97	1.64	2.21	2.0	1.106	0.010	55.0
	F (ppm)	0.0-3.08	0.75	2.81	0.78	3.0	0.045	0.024	56.0
Western wheatgrass	B (ppm)	3.11-14.6	8.36	1.42	0.08	10.0	0.003	0.0008	42.0
	Mo(ppm)	0.28-1.16	0.52	1.39	0.38	4.0	0.004	0.001	40.0
	F (ppm)	0.0-4.81	0.82	3.83	0.61	3.0	0.088	0.037	43.0

The observed error variance, E_s, is found by:

$$E_s = \frac{S_b^2}{N_b} + \frac{S_c^2}{N_b \cdot N_c} + \frac{S_d^2}{N_b \cdot N_c \cdot N_d} + \frac{S_e^2}{N_b \cdot N_c \cdot N_d \cdot N_e} \qquad (9)$$

where N_b to N_e are the number of nested levels at each of the sublevels of the model.[2] If E_r is greater than E_s, a reproducible map can be drawn of the study area.

The variance mean ratio (V_m) is used to determine the stability of maps derived from the grid data.[2] If V_m is equal to 1.0, gross difference can be shown, and if V_m is 3.0 or greater a geochemical map is quite stable and representative of the actual distribution. Generally, the number of samples required for a stable map is 2-4 samples per square mile. The grid sample program for C-a was 221 samples/48 sq mi. These are actually 4.4/sq mi if the grid were extended to infinity. The 1/2 mile grid interval was again confirmed as a reasonable balance between need and analytical capability. Tables 3, 4, 5, 6 contain the variance ratio (V), the required number of samples per square mile for a stable map (N_r), the maximum permissible error variance (E_r), the observed error variance (E_s), and the number of samples analyzed at this point in time in the studies.

As examples of maps derived from this data, Figures 7 and 8 are trend surface maps of the grid samples for Mo in soils and Big sage for Tract C-a and vicinity. Most constituents analyzed in the surface soils and sage exhibit a regional variance component. Mercury, B, and soil pH have a greater proportion of the variance at more local levels and in the case of Hg, at the analytical level. When mapping soils on a basinwide scale and computing means for supertownships (144 sq mi) it is possible to map Zn (Figure 3), but on the local scale (48 sq mi), it is not possible to map soil Zn (N_r in Table 3) using individual samples collected on a 1.2 mile grid. Figures 9 and 10 are hand contoured maps of the grid samples for Mo in soils and Big sage for Tract C-b and vicinity. These figures are included as examples of the application of the data. Additional maps for other constituents and a more detailed discussion including the relationships to the geology of the area are contained in the theses by Candito[6] and Zuccaro.[7]

SUMMARY

Trace element baselines are being established for surficial materials in the Colorado oil shale region. The sampling of such large volumes of materials dispersed over large areas presents special problems in sampling. A two-stage sampling procedure employing hierarchial analysis of variance has been employed to establish reliable estimates of means, deviations and expected ranges for trace elements in soils, stream sediments, and plants of the area. The analysis of variance technique allows the determination of a sampling interval which allows the mapping of the distribution of trace elements that is not an artifact of the sampling. Sample design allows the

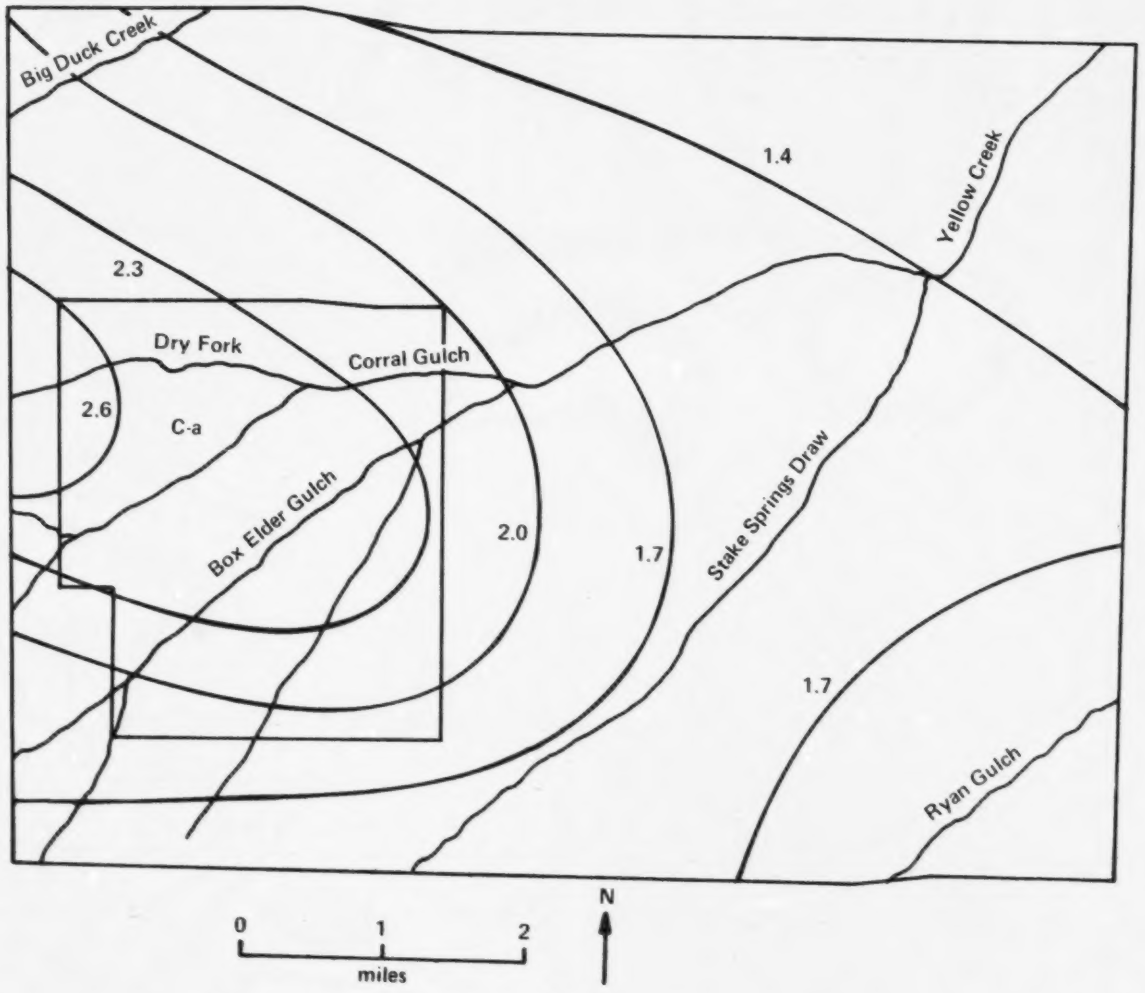

Figure 7. Mo (ppm) in Surface Soils of Tract C-a and Vicinity.

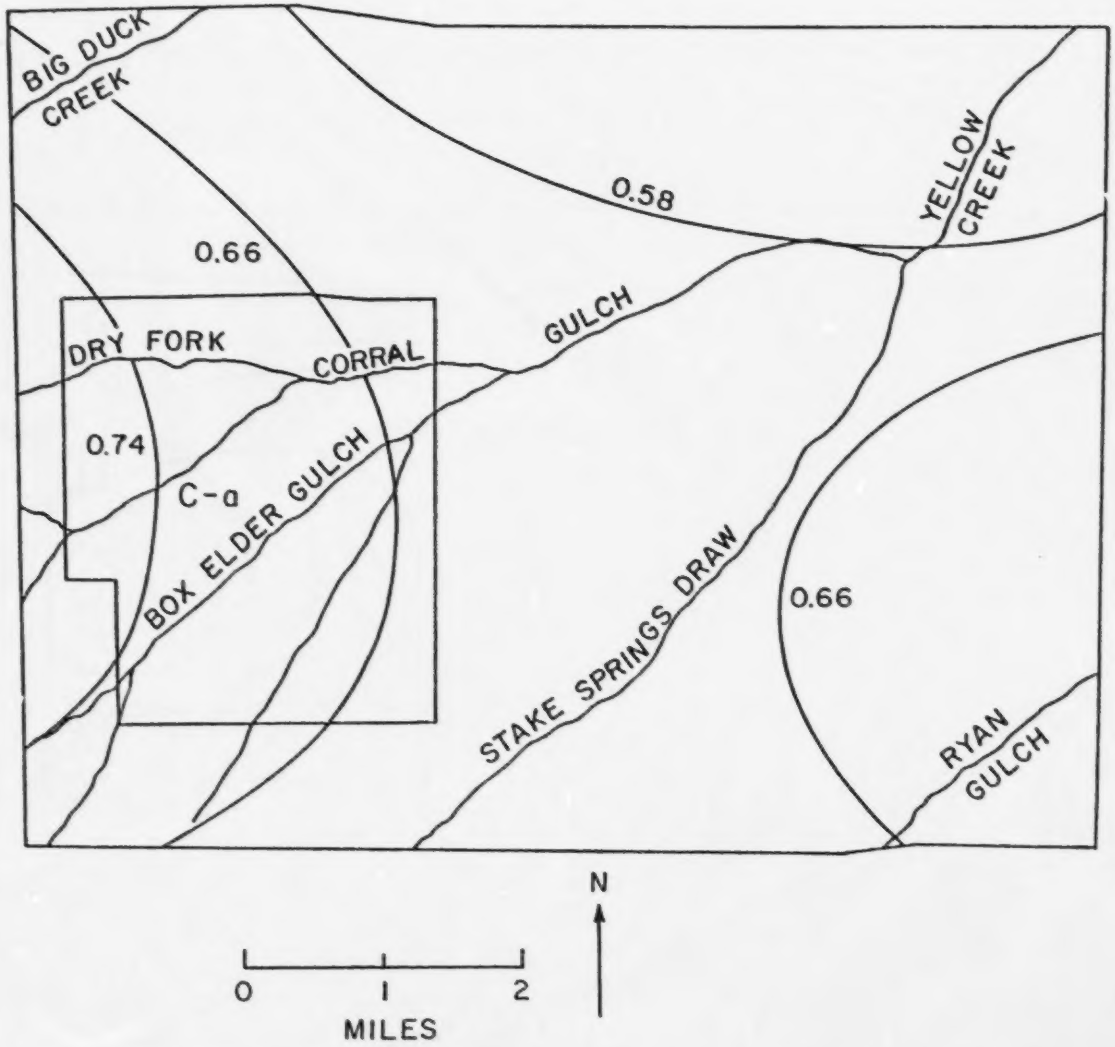

Figure 8. Mo (ppm) in Big Sage of Tract C-a and Vicinity.

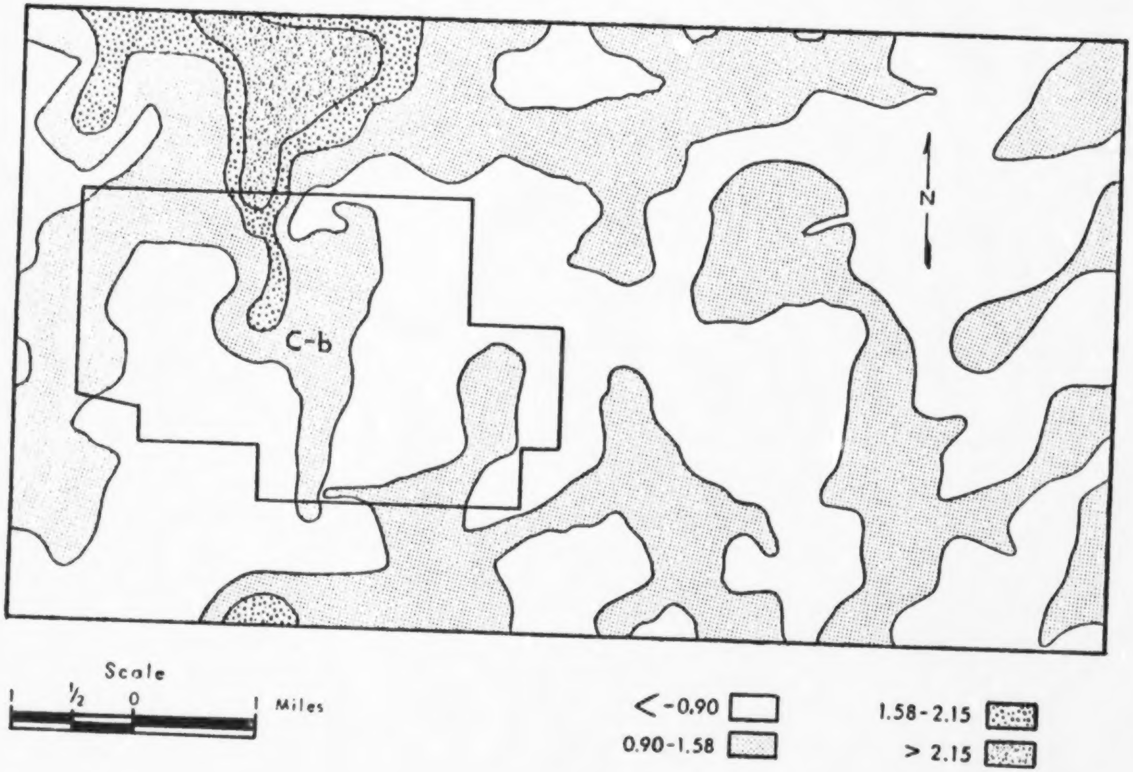

Figure 9. Mo (ppm) in Surface Soils of Tract C-b and Vicinity.

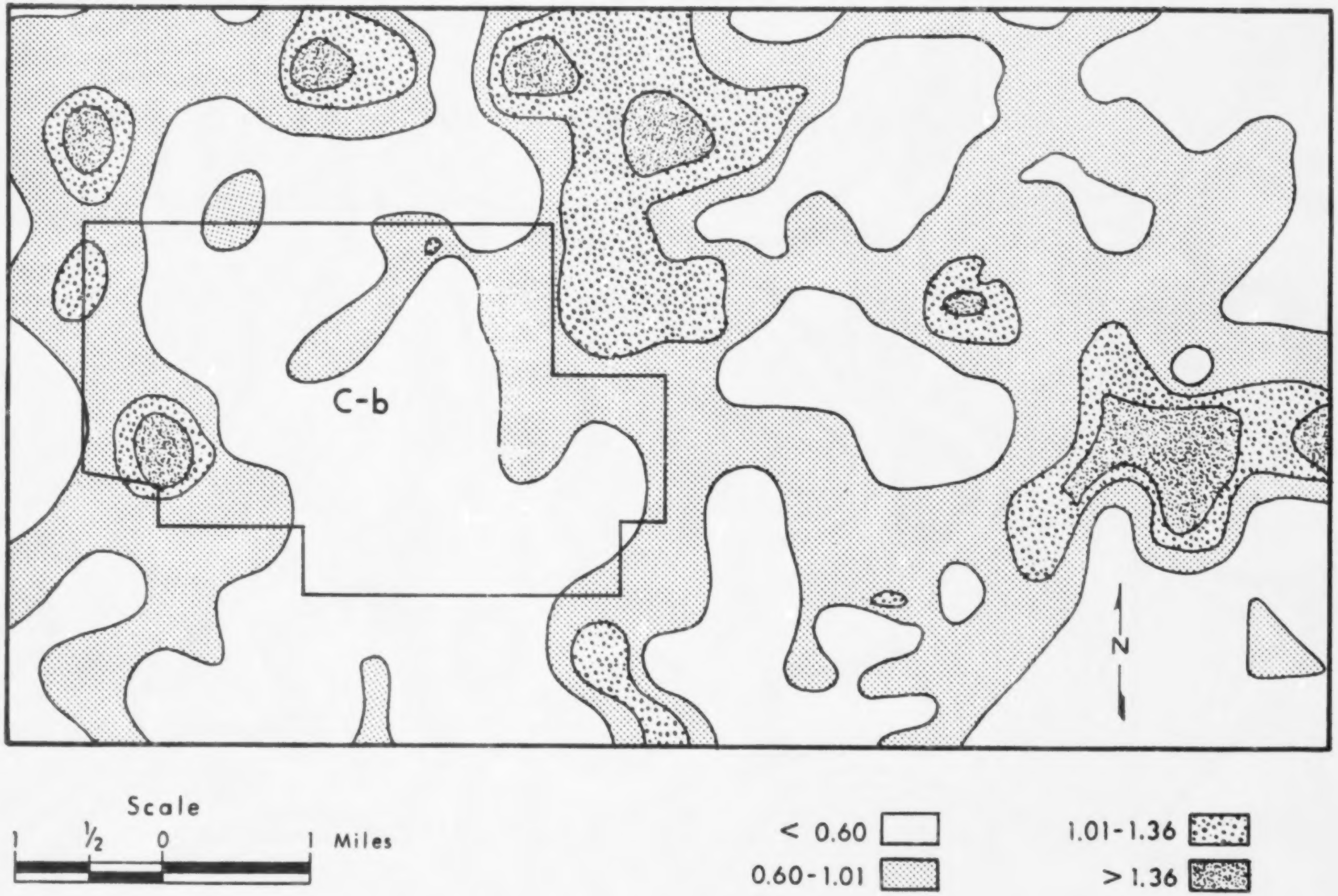

Figure 10. Mo (ppm) in Big Sage of Tract C-b and Vicinity.

determination of reliable baselines upon which the prediction of future impact and the measurement of actual impact can be measured.

ACKNOWLEDGEMENTS

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AMBIENT AIR SAMPLING AND ANALYTICAL PROCEDURES FOR OIL SHALE DEVELOPMENT AREAS

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ABSTRACT

Quality Assurance criteria are used to evaluate sampling and analytical procedures and assess methods for measurement potential in ambient air that is relatively clean. Precision and accuracy of sampling and analytical procedures are used to place methods in three categories: Most reference and equivalent or compliance methods are in category 1. Category 2 contains those methods which are recognized in the literature and have a relatively high frequency of use. Promising methodology is discussed as a third category, although an indepth selection of these relatively new methods has not been included in the procedures presented for measurement of ambient air pollutants anticipated in oil shale development.

Ambient Air monitoring objectives are discussed by analyzing the requirements of developing baseline concentrations and air quality parameters. Standards, sampling sites, meteorology, and modeling, and selection of procedures are seen as controlling factors in developing data in the low concentration range of pollutants of oil shale development Areas in the West.

(Paper presented at Symposium but not submitted for publication in the Proceedings. For more information, contact the author.)

EPA R&D EFFORTS IN THE DEVELOPMENT OF OIL SHALE
LUNCHEON ADDRESS

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Our Nation came to believe, without question, that investment of money and labor to develop natural resources would be rewarded by a growing economy. The inherent limitations to this traditional wisdom have now been demonstrated. We know that in the short term the cost of energy--that is the capital and labor required to produce usable energy--will increase.

Furthermore, the potential environmental problems of oil shale, coal and nuclear energy are much greater than those of petroleum and natural gas, and will require increased expenditures if they are to be solved.

Although we have all witnessed some of the near term economic, political and environmental implications of the closing of the petroleum age, none of us can forecast accurately what the future has in store. The energy crisis may mean a protracted and gradually worsening economic recession, lack of opportunity for our young people, and decreasing social mobility. It may mean rapidly degrading environmental quality and exhausting our supplies of clean air, clean water, and productive land.

On the other hand, the cost of energy may rise to the point where widely available and environmentally benign sources will be used to meet society's economic and social needs.

Let me try to give you some perspective on the size of the environmental impact that a substantial oil shale industry may have. Assuming that oil shale will yield 25 gallons of crude oil for each ton of rock refined, we will need to process a weight of shale that is one and one-half times as much as the weight of coal we presently mine to produce the crude oil we currently import. If we are really to use the 600 billion barrels of crude oil that are potentially available in the Green River shale formation, we will have to divert enormous resources of land, capital and labor.

The major environmental problems include the large quantities of dust from the mining operations, airborne emissions from retorting processes, and the large amounts of spent shale.

The oil shale industry will be located in the semiarid region of the Colorado River Basin where the demand for a limited water supply is already critical. Oil shale processing and the revegetation of spent shale will consume large amounts of water, a critically limited resource.

There is concern that the leaching of the soluble salts will increase the salinity of streams and groundwater. Potentially toxic runoff from spent shale could also threaten public health.

The data on which we base these environmental concerns is limited to pilot plant experience. As we develop full scale production, new and certainly equally significant problems will become apparent.

Control technology can minimize the environmental impact of energy conservation processes. Regulations can prevent pollutants from causing serious and widespread environmental degradation. Establishment of such standards requires a constant and careful evaluation of existing technologies. Some important questions, however, must be asked: Will control technologies reduce pollutants to acceptable levels? What are the realistic costs of these controls, both in dollars and in energy loss? Where is the balance between energy losses and environmental gains?

Ideally, with the potential evolution of conversion processes and their "built-in" environmental controls, an energy conversion technology may evolve that is both economically and environmentally sound.

In the final quarter of the 20th century the focus is shifting to the development of a "total program." Environmental controls are developed concurrently with our new energy industries. The result is inherently cleaner than our previous after-the-fact practices.

Advanced fossil fuel environmental control technology is the key tool necessary to bring about the total program for oil shale conversion. Such a program requires both commitment and cooperation from the industrial developers, the environmental researchers and regulatory agencies. Successful development of environmental controls concurrent with development of energy production processes will avoid the more costly and less efficient task of reconfiguring the technology.

EPA AND THE FEDERAL ENERGY/ENVIRONMENT RESEARCH AND DEVELOPMENT PROGRAM

The Federal Interagency Energy/Environment Research and Development Program is an 11 agency effort committed to energy development with environmental protection. Major program goals are to:

- Safeguard health and the environment without unduly delaying the accelerated development and use of domestic energy resources.
- Anticipate environmental impacts of energy conversion technologies and stimulate the development of cost-effective environmental controls.
- Promote the transfer of energy-related environmental information.

The Office of Energy, Minerals, and Industry (OEMI), within EPA's Office of Research and Development, plans and coordinates this Interagency Program. Through this program, OEMI provides support to numerous other Federal agencies including the Department of Energy (DOE) and the National Institute for Occupational Safety and Health (NIOSH).

FY-78 Interagency Program funding was $100 million, of which $26 million was passed on by EPA to other Federal agencies. This funding supports a number of energy-related programs, including characterization and monitoring of pollutants, transport processes, ecological effects, health effects, integrated assessment studies and environmental control technology.

In October 1978 the headquarters office of OEMI and its Cincinnati Laboratory (IERL) initiated a closer working relationship between EPA and the industrial firms interested in developing oil shale. Two meetings were held with industry to gather ideas on the environmental and regulatory problems that must be faced prior to bringing oil shale to production. On January 23-24, 1979, in Denver, senior management from EPA's Office of Energy, Minerals, and Industry, representing the R&D effort, and Region VIII, representing the regulatory function met with top management from 25 companies. Management from DOE and DOE's Area Oil Shale Office were also in attendance. Industry heard both DOE and EPA express a positive attitude towards the prospect for oil shale commercialization. The industry representatives were encouraged by the idea of cooperative research.

EPA Research

EPA's commitment to cooperative research has been to provide funding for research on the following topics: characterization and control of retort emissions, solid waste handling, revegetation, ambient air quality and groundwater pollution.

Technology Transfer

EPA-IERL-CI is assembling the Pollution Control Guidance Document for Oil Shale Development. This document will be EPA's policy defining "good environmental practice" at this stage of the industry's development. Sections include sampling, analysis and monitoring of emissions, effluents, and solid wastes; and suggested interim standards for air emissions, water effluents and solid waste disposal for the major retorting processes. Also included are discussions of state-of-the-art of oil shale development; procedures for air monitoring; applicable Federal, state, and local laws and regulations; analytical procedures and quality assurance manuals; and a catalog of existing Federal, state, and locally required permits.

This Oil Shale Symposium on Sampling, Analysis and Quality Assurance is an important part of a major effort underway to make America less dependent on foreign sources of energy. In the years to come, the Nation must conserve the energy it has, harness new sources, and work to develop the energy resources already identified, including its vast oil shale deposits. Efficient, economical ways of extracting energy from these resources must be developed while, at the same time, giving full credence to the basic imperative that energy resource development cannot come at the expense of the quality of our health or of the natural environment.

Providing the pollution control guidelines that can grow with the industry and its technology is a novel concept. This symposium focuses on the research necessary to define the environmental part of the oil shale production processes.

We thank you for your contribution to this effort.

A CONCEPTUAL MODEL FOR AN INTEGRATED ENVIRONMENTAL ANALYSIS ON OIL SHALE TRACT C-b

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ABSTRACT

In accordance with lease stipulations requiring that system interrelationships be addressed in the environmental baseline program, a conceptual model of the oil shale Tract C-b ecosystem was developed around 2.5 years of hydrological, meteorological, and ecological baseline data. A systematic procedure was used to organize, classify, summarize, integrate, and synthesize the baseline data into categories of key ecosystem components and processes. The operator's detailed development plans for the oil shale were used to identify anticipated perturbations to the ecosystem. These perturbations were integrated into the conceptual model along with the key components and processes. Volume 5 of the final report for the Environmental Baseline Program serves six purposes: (1) it summarizes most baseline information in nearly 500 time-series graphs that depict behavior of many components and processes in the ecosystem measured during the 2.5-year period; (2) it serves as a cross-reference to other volumes in the report; (3) it develops a conceptual model of the Tract C-b ecosystem; (4) it permits users to track potential impacts qualitatively through the ecosystem using this conceptual model; (5) it assists users in planning a monitoring program; and (6) it assists in planning mitigation of potential impacts.

INTRODUCTION AND BACKGROUND

This paper describes why and how a conceptual model was constructed to integrate engineering plans for oil shale development with environmental baseline data on Tract C-b. The model is useful for various types of environmental analyses, such as tracing potential impacts through the ecosystem, planning monitoring, and developing mitigation measures.

The C-b Tract

Oil Shale Tract C-b is a Federal Lease Tract of approximately 5,100 acres located in the Piceance Basin, Rio Blanco County, Colorado. Development of Tract C-b is governed by terms and conditions of the Federal Oil Shale Prototype Leasing Program administered by the Area Oil Shale Supervisor, Geological Survey, U.S. Department of the Interior. The environmental stipulations attached to the Federal Oil Shale Lease require that a two-year environmental baseline field study be conducted on the tract and 1-mile surrounding area prior to oil shale development.

The study, the Tract C-b Environmental Baseline Program, was initiated on 1 November 1974 and completed on 31 October 1976. Although this was the official period of investigation, some data were collected as early as July 1974 and as late as November 1976.[1] The total period of data collection, therefore, was about 2.5 years. During this period, data were collected and analyzed on surface water, groundwater, air quality, meteorology, flora and fauna, soils, geology, and archeology.

Development of the tract is by C-b Shale Oil Venture of Ashland Oil, Inc., and Occidental Oil Shale, Inc., operator.

Ideal Baseline Studies

Under ideal conditions, environmental baseline field studies would be guided at the outset by a conceptual, and possible mathematical, model that identifies the most important ecosystem components and processes to measure. After a thorough literature search combined, perhaps, with some field reconnaissance, a preliminary model would be developed to identify gaps in existing data and information about key indicator variables and ecosystem stress points.

Only then would extensive field studies be planned and implemented. Data from these studies would feed back to the modelers, who would revise the model and identify areas where the field program needs to be revised, etc. Ideally, this iterative cycle between model and field studies would continue without interruption into a monitoring and mitigation phase throughout the life to the project.

In the case of Tract C-b, environmental baseline field studies were begun much before the engineering plans were complete. The field studies were conducted by experts in many disciplines, each working generally without regard for interrelationships between contiguous disciplines and beyond.

Finally, after 2.5 years of baseline studies and major revisions in the oil shale operator's detailed development plan, the conceptual modeling began, largely to satisfy a clause in the oil shale lease requiring that system interrelationships be addressed. The results of that modeling effort appeared as Volume 5 of the Environmental Baseline Program Final Report.[1] Much of the remainder of this paper discusses the philosophy and methods of that conceptualization effort.

SYNTHESIS OF BASELINE STUDY INFORMATION

The fundamental challenge was to portray ecosystem interrelationships on Tract C-b, based on a 2.5-year plethora of data that had been collected somewhere on or near the tract at different times and different locations. The challenge was met by viewing the problem in a systems perspective and using the tool of a dynamic model to assist in organizing ideas and information.

Models and Modeling

Modeling means many things to many people. In its broadest sense, we all model whenever we think: we abstract in our minds essentials from the real world, analyze the situations, decide on the basis of our conceptual understanding (our "mental model"), and act on that decision.

More formally, modeling means documenting our abstract thinking. For example, models can take the form of three-dimensional objects (working models, scale models), two-dimensional representations of the three-dimensional world (engineering drawings, topographic maps), simple narrative statements, more abstract conceptualizations of real-world interrelationships (diagrams, matrices, and equations), and computer programs that solve those equations.

In general, a model is simply a way of organizing, classifying, summarizing, integrating, and synthesizing information about the real world, usually in order to reach some conclusions or decisions about that world.

A Systems Viewpoint

A system is a collection of objects which, by their interaction and interdependence, form an entirety that functions in a particular way. Often components of that entirety interact to confer on the system certain emergent properties that might not readily be inferred from a study of the component parts separately; first-, second-, and higher-order interactions between and among components cause the system to behave uniquely as a functional unit, rather than as the simple sum of all the component activities. In other words, because of synergistic effects, the system takes on behavioral characteristics that transcend the characteristics of its component parts.

Components of a system are called variables, because they vary through time and space. Usually variables are of two types: driving variables and state variables. Driving variables provide input to the system from outside; in a sense, they "drive" the system. These components are external to the system in that they affect the ecosystem without themselves being affected by it.

Components that influence each other through abiotic or biotic feedback are called state variables. These components are within the system, and their condition reflects the state of the system at any given time. State variables interact with each other sufficiently to affect each other's behavior.

In living systems, variables are linked to each other by flows of matter or energy, and they interact with each other through these flows. Certain system processes act as valves to regulate the flows: as the rate of a process changes, the flow rate changes, and the state variable dependent on that flow is affected, thus becoming an indicator of the change. Processes are regulated by driving variables and, often through feedback, by state variables.

The Ecosystem

In ecology, a system may be an organism, a species population, or a total ecosystem. We were concerned with a complex of ecosystems that make up Tract C-b and its immediate vicinity. The ecosystems on Tract C-b are more or less naturally evolved collections of living things interacting with each other and with their nonliving environment to form recognizable units characterized by unique emergent properties.

In an ecosystem, driving variables are usually natural abiotic components. Examples are insolation and precipitation. However, they also include certain man-influenced inputs, such as pesticides, herbicides, grazing management, or influences deriving from such activities as oil shale development.

State variables are chosen to describe the ecosystem of interest as economically as possible. A state variable could be a single species of plant, a life form (grass, forb, shrub, tree, etc.), or even all plants in the system. Selection of state variables depends on the level of resolution at which we want to describe the system and on the importance of each component.

Common processes in ecosystems are photosynthesis, respiration, birth, death, etc. Thes example processes control the flow of carbon through the system. Other processes regulate other flows.

METHODOLOGY FOR CONCEPTUALIZATION

Our synthesis activity took place concurrently with that of the development of four other volumes summarizing 2.5 years of baseline studies on the tract. These covered regional and temporal setting (Volume 1), meteorology, air quality, and noise (Volume 2), hydrology (Volume 3), and ecology (Volume 4).

We had several opportunities to meet with the field investigators as they wrote and revised drafts of the above volumes. One of us (Van Dyne) also viewed the tract, both by air and on the ground, to develop a general impression of the system under consideration.

First we attempted to define ecosystem response units of landscape on the tract and to identify the main abiotic, autotrophic, and heterotrophic components in each unit. Then we focused on currencies flowing through these components. Next, we identified the physical and biological processes responsible for these flows. Finally, we examined the factors controlling these flows, considering those occurring naturally in the environment and those related to potential oil shale development.

Interpretation of the baseline data and information of earlier volumes was governed by simple modeling criteria: to identify and describe interrelationships within the tract's environmental system, it was necessary to systematically organize an extremely large data base in order to minimize loss of information, and to rationally reduce that data base to a workable size.

A method of interactive functional aggregation was used to combine ecosystem components, ecosystem processes, and oil shale development activities into manageable groups or classes. However, before important components could be identified and chosen for subsequent discussion from among innumerable driving and state variables, some selection criteria were necessary.

Choice of driving variables and abiotic state variables (e.g., soil moisture) was governed by the importance of these variables in the baseline studies and through discussions with principal investigators for the various disciplines. The biotic state variables were grouped according to their functional roles in the ecosystem (e.g., trophic level, life form). We used a principle of inclusivity in defining biotic state variables: the objective was to include 90 to 95 percent of any trophic group, by biomass, within the component categories. Some specifics follow.

Ecosystem Response Units (ERU)

An ecosystem response unit is a geographical, or spatial, unit that (1) possesses common vegetative, topographic, elevational, and edaphic (or aquatic) characteristics, and (2) responds to environmental influences more or less uniformly throughout. Effectively, response units are considered to be small ecosystems within the larger environmental system of the entire tract area.

The 13 ecological communities predominant on the site were aggregated into five ERUs, primarily on the basis of common vegetative physiognomies and topographic locations (Table 1). The vegetation provides an excellent link between the abiotic components and the animals. When integrated into plant-animal-topographic response units, these functional spatial units are considered as small ecosystems that constitute the large environmental system of Tract C-b.

Upon this natural environmental system, two additional ERUs are being imposed by oil shale development: upland rehabilitated sites and bottomland rehabilitated sites.

TABLE 1. AGGREGATIONS OF PLANT COMMUNITIES INTO ECOSYSTEM RESPONSE UNITS FOR A CONCEPTUAL MODEL OF THE C-b SYSTEM[a]

Plant Community/ Habitat Types	Corresponding Ecosystem Response Unit	Subscript 1
Piñon-Juniper	Upland Forest	1
Chained Rangeland Bunchgrass Sagebrush Mountain Shrub	General Upland	2
Rabbitbrush Greasewood Sagebrush Wildrye Riparian	General Bottomland	3
Meadow	Meadow	4
Stream Pond/Marsh	Aquatic	5
	Upland Rehabilitated	6
	Bottomland Rehabilitated	7

Ecosystem Components

The next major step was to identify all the state and driving variables that might be important. For Tract C-b this required reviewing and reorganizing species lists and vegetative communities into functional components at a medium level of resolution. (The level of resolution is the degree to which component parts are combined or separated, hence, the amount of detail presented). This time-consuming process required interactive consultations with disciplinary specialists to determine which species could be aggregated into which groups in a reasonable way.

In addition, different ecosystem components occur in different ERUs; where possible, data were used to associate specific components with ERUs. In some cases, as with driving variables, a component occurs in all ERUs.

From an original list of 47 possible driving variables on the tract, 15 were chosen for the model. They are classified as climatic, resource management, or oil shale development variables. Natural driving variables of the system include precipitation, air temperature, wind, and solar radiation. Management variables are forest cutting and livestock grazing. Emissions and other disturbances are included as oil shale development variables.

The 240 species of vascular plants on the site were classified first by life form: trees, shrubs, annual grasses and forbs, perennial graminoids, and perennial forbs. Similarly, the 168 vertebrate animals on the tract were aggregated first by taxonomic category (shrews, bats, ungulates, etc.), then more broadly (small, medium-sized, and large mammals, waterfowl, etc.), and again by function (omnivore, carnivore, herbivore, etc.).

The final aggregate grouping of state variables is presented in Table 2. Subsystems are based on flow currencies, which are explained below. Acronyms are used for rapid identification in model diagrams. The $\underline{I}$ subscripts refer to ecosystem response units in which a variable is found (Table 1); the $\underline{J}$ subscripts are the life forms of the plants and animals in the model.

Time Dynamics

A primary concern of the ecosystem analyst is the behavior of system components and processes through time. By tracking time-variant behavior of several related components and processes it is often possible to infer cause-effect relationships through statistical analysis. Understanding such relationships is fundamental to sound modeling.

For this reason, virtually all data for driving variables and state variables from Tract C-b were plotted, wherever possible, against a uniform 2.5-year time scale. Unfortunately, time and funding did not permit rigorous statistical analyses, but even when statistical correlations are not determined, information about how a given ecosystem component or process varies over time is valuable.

If we can assume that a time-variant annual curve somewhat represents the norm for a given variable, we can then hypothesize certain interrelationships that affect the behavior of that curve. To this end, nearly 500 time-series graphs of driving variables, state variables, and ecosystem processes were drawn in a standard format.

Ecosystem Flows

One of the main reasons for identifying ecosystem components by their function, rather than by taxonomic classification, is that a functional classification helps us understand the interrelationships in the system, and thus how the system works. For example, the movement of carbon is one way of tracing interrelationships among the abiotic and biotic components of the system. Carbon, then, is considered a flow currency; i.e., it is a common element that flows between ecosystem components as a direct result of certain processes associated with the functioning of those components.

TABLE 2. IMPORTANT STATE VARIABLES IDENTIFIED ON TRACT C-b

The initial letter of each acronym refers to the flow currency of the subsystem in which that variable appears. Subscripts are explained in the text.[1]

Subsystem Title and Abbreviation	Aggregate State Variable Name	Acronym	Limit I	Limit J
Animal Population (P)	Source	PSS		
	terrestrial animal numbers	PTA (I, J)	5	10
	aquatic vertebrate numbers	PAV (I)	2	
	aquatic invertebrate numbers	PAI (I)	2	
	sink	PASS		
Animal Weight (G)	source	GSS		
	terrestrial animal weights	GTA (I, J)	5	10
	aquatic vertebrate weights	GAV (I)	2	
	aquatic invertebrate weights	GAI (I)	2	
	sink	GSS		
Carbon Biomass (C)	Source	CSS		
	live shoots	CVS (I, J)	7	5
	live roots	CVR (I, J)	7	5
	standing dead	CVD (I, J)	7	5
	aboveground litter	CLA (I)	5	
	belowground litter	CLB (I)	5	
	aquatic rooted plants	CAR (I)	2	
	aquatic unrooted plants	CAN (I)	2	
	aquatic detritus	CAD (I)	2	
	sink	CSS		
Heat (H)	source	HSS		
	soil top layer head	HST (I)	5	
	soil bottom layer heat	HSB (I)	5	
	aquatic to layer heat	HAT (I)	2	
	aquatic bottom layer heat	HAB (I)	2	
	sink	HSS		
Water (W)	source	WSS		
	surface water (snow, ice, rain)	WSI (I)	5	
	top soil water	WTS (I)	5	
	bottom soil water	WBS (I)	5	
	groundwater layer	WGR (I)	5	
	aquatic ice layer water	WAI (I)	2	
	aquatic water	WAW (I)	2	
	sink	WSS		
Acreage (A)	surface area	ACR (I)	12	

The flow rates of currencies through an ecosystem control the rate of growth or decay of any particular ecosystem component, for it is these currencies (carbon, phosphorus, nitrogen, etc.) that are stored or disseminated. The flows themselves, however, are simply the reflection of various processes that actually control the rates of flow. For example, one of the processes that controls biomass flow from generation to generation is reproduction.

Criteria for selecting currencies of flow were (1) broad commonality among many system components and (2) ease of measurement. Six currencies were used in developing the conceptual model: population numbers for various animals, weights of individual animals, biomass of plant and litter components, temperature of soil layers, water content of various terrestrial and aquatic subdivisions, and surface land area.

Ecosystem Processes

After the flow currencies and components were chosen, the processes that control the flows were identified and similarly aggregated or separated, according to their importance within the level of resolution specified. The choice of these was constrained by the baseline information available and by considerations for future monitoring.

By regulating flow rates, the physical, chemical, and biological processes that transfer matter and energy among components of the ecosystem account for the dynamics of the state variables. Through successive analysis and synthesis, a total of 85 terrestrial and aquatic ecosystem processes were identified as important on Tract C-b.

These processes were associated with the six flow currencies. The currencies formed the basis for developing six conceptual subsystems (Table 2) within the model. Each subsystem tracks the flow of a particular currency among ecosystem components, and subsystems are linked to each other conceptually by flows of information between subsystems. Figure 1 diagrams carbon, heat, and water subsystems on the tract. Table 3 lists ecosystem components and processes associated with each subsystem in Figure 1. Information linkages between the heat subsystem and other components and subsystems are illustrated in Figure 2. Sympols are explained in Figure 3.

Oil Shale Development Influences

Because the dynamics of system variables are controlled by the processes, anything that affects those processes will affect the state variables indirectly. In addition, state variables can be affected directly by certain outside influences. For example, bulldozing trees to develop a road is a direct effect. The process of erosion is affected indirectly as bulldozing uncovers and loosens the soil. The interaction of bulldozing and precipitation accelerates the erosion rate and thus the flow (or loss) of soil.

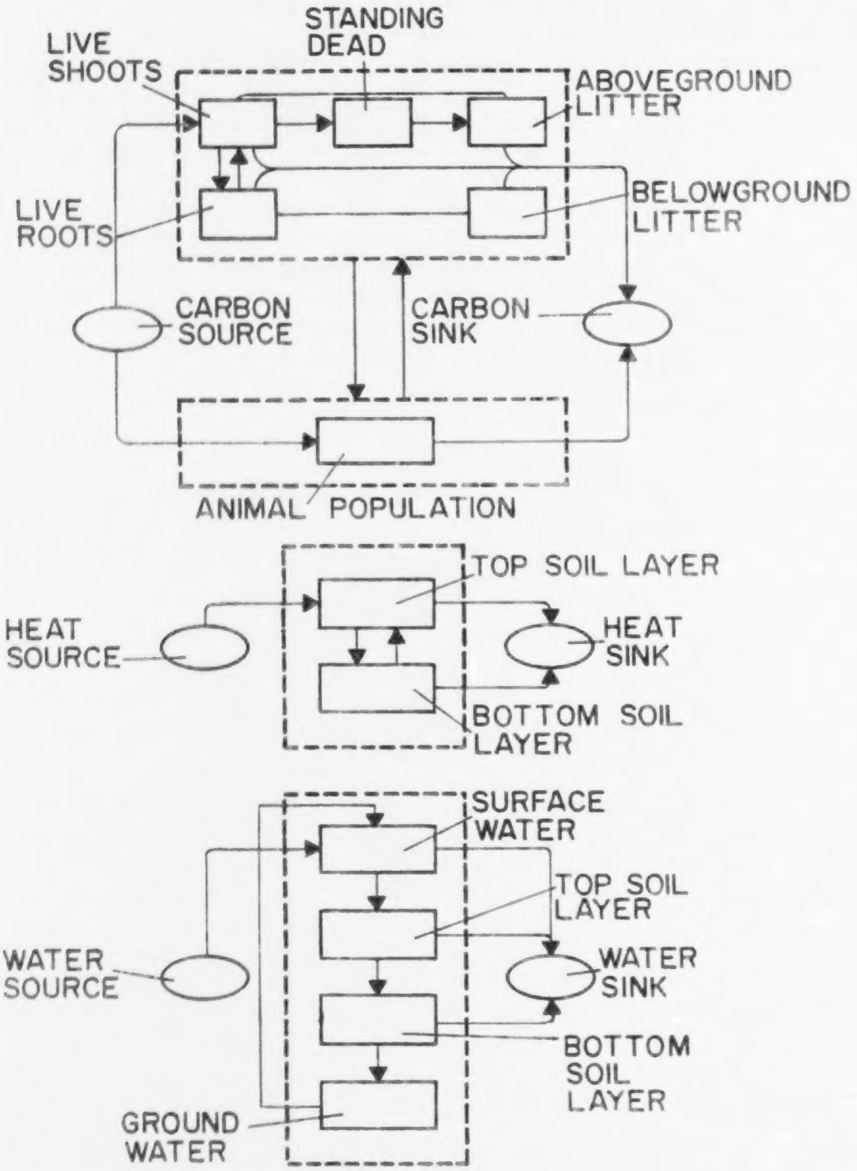


Figure 1. A simplified conceptual diagram of flows within the carbon, heat, and water subsystems.[1] Carbon flows are through both plant and animal subsystems.

TABLE 3. ECOSYSTEM PROCESSES CONTROLLING FLOWS IN THE CARBON, HEAT, AND WATER SUBSYSTEMS ON TRACT C-b[1]

Flow Currency	Ecosystem Components		Ecosystem Processes
	From	To	Process
Carbon	Carbon source	Live shoots	Photosynthesis
	Carbon source	Aboveground litter	Excretion input
	Carbon source	Aboveground litter	Dead animal input
	Live shoots	Live roots	Translocation to roots
	Live shoots	Standing dead	Shoot death
	Live shoots	Aboveground litter	Shoot shattering
	Live shoots	Carbon sink	Shoot respiration
	Live shoots	Carbon sink	Shoot grazing output
	Live roots	Live shoots	Translocation to shoots
	Live roots	Belowground litter	Root death
	Live roots	Carbon sink	Root respiration
	Live roots	Carbon sink	Root grazing
	Standing dead	Aboveground litter	Dead shattering
	Standing dead	Carbon sink	Dead grazing
	Aboveground litter	Carbon sink	Aboveground decomposition
	Aboveground litter	Carbon sink	Aboveground litter grazing
	Belowground litter	Carbon sink	Belowground litter grazing
	Belowground litter	Carbon sink	Belowground litter grazing
Heat	Heat source	Top soil layer	Radiation
	Heat source	Top soil layer	Convection in
	Top soil layer	Bottom soil layer	Conduction down
	Top soil layer	Heat sink	Reradiation
	Top soil layer	Heat sink	Convection out
	Bottom soil layer	Top soil layer	Conduction up
	Bottom soil layer	Heat sink	Conduction down
Water	Water source	Surface water	Precipitation
	Surface water	Top soil water	Snow melt/infiltration
	Surface water	Water sink	Surface evaporation
	Top soil water	Bottom soil water	Percolation
	Top soil water	Water sink	Top soil evaporation
	Top soil water	Water sink	Upper soil transpiration
	Bottom soil water	Groundwater layer	Percolation
	Bottom soil water	Water sink	Lower soil transpiration
	Groundwater layer	Surface water	Springflow

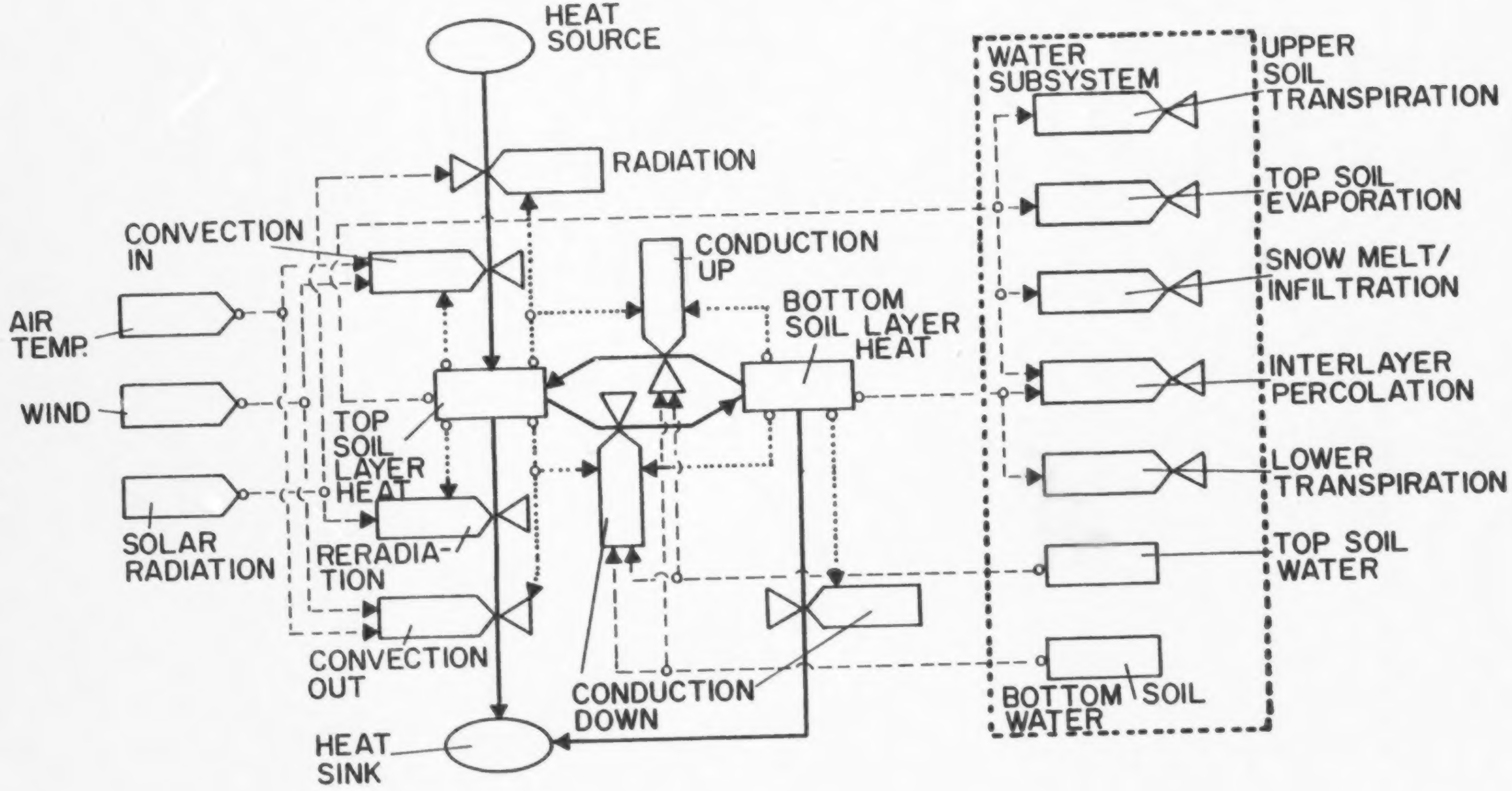
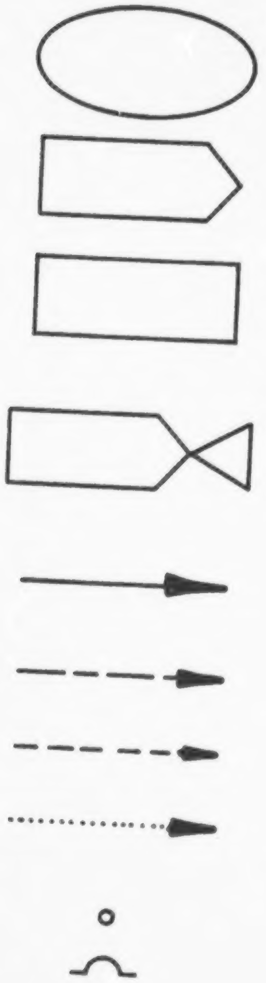


Figure 2. Partial system control diagram of heat subsystem on oil shale Tract C-b. (Modified from Van Dyne and Haug.[1]) Symbols are explained in Figure 3.[2]



Source or sink.

Driving variable.

State variable (ecosystem component).

Process. These may be thought of as valves that control the flows of matter or energy through the subsystem.

Materials or energy flow. Denoted by a solid line.

Information flows. Dots and dashes represent input from driving variables. Dashes trace the inter-subsystem influences of state variables on processes. Dots are the intra-subsystem feedback loops through which state variables influence processes within their own subsystem.

Takeoff points and crossings. The small circles represent take-off points or branches in information linkages. The other symbol simply denotes a crossover.

Figure 3. Symbols and conventions used in system control diagrams.[2]

Major Activities	Oil Shale Development Phases				
	Phase 1 Site Preparation	Phase 2 Preproduction Mining	Phase 3 Ancillary Facilities	Phase 4 Commercial Facilities	Phase 5 Operation
Build/Extend Roads	X		X	X	
Build Impoundment(s)	X	X			
Sink Shafts		X	X	X	
Mine (Development/Retort Construction)		X	X	X	X
Construct Underground Facilities			X	X	
Construct Surface Facilities			X	X	
Process Raw Materials/ Operate			X		X
Build Power Transmission Line(s)			X		
Build Staging Area (off-tract)			X		
Build Pipelines (off-tract)			X		
Build Commercial Facilities				X	

Figure 4. Development Matrix. Oil Shale Development Phases and their Associated Major Activities[1]

SUB-ACTIVITIES THAT PRODUCE ENVIRONMENTAL PERTURBATIONS	Major Activities										
	Build/Extend Roads	Build Impoundments	Sink Shafts	Mine	Construct Underground Facilities	Construct Surface Facilities	Process Raw Materials/Operate	Build Power Transmission Lines	Build Staging Area (off-tract)	Build Pipeline(s) (off-tract)	Build Commercial Facilities
Remove Vegetation	X	X	X			X		X	X	X	X
Store Equipment/Vehicles	X	X	X		X	X			X	X	X
Operate Equipment	X	X	X	X	X	X	X	X	X	X	X
Drill and Blast	X	X	X	X	X	X	X	X	X	X	X
Grade (Excavate & Fill)	X	X			X	X		X	X	X	X
Dispose of Waste	X	X	X	X	X	X	X		X	X	X
Pave or Surface	X	X				X			X		X
Fence	X	X	X			X			X		X
Increase Traffic	X					X			X		X
Disturb Vegetation	X	X	X			X		X	X	X	X
Build/Extend Roads		*	*			*		*	*	*	*
Remove Underground Water (dewater)			X	X	X		X				X
Dispose of Water			X	X	X		X				X
Sink Shafts				*							
Build Conveyor				X							
Operate Conveyor				X			X				
Crush Mined Shale				X			X				
Erect Structures					X	X		X	X		X
Exhaust Retorting Gasses							X				

*Road building or sinking shafts can be considered either major activities or subactivities.

Figure 5. Activity matrix. Subactivities associated with major oil shale development activities.[1]

To determine the effects of oil shale development on Tract C-b it was necessary to systematically identify those effects that might be direct and those that might be indirect. Three successive matrices were used to do this, all derived from the operator's detailed development plan and its modification.

The first matrix associates major activities of oil shale development with phases of development (Figure 4). Each major activity is then related to subactivities within a second matrix (Figure 5). Each of these subactivities generates certain environmental perturbations or impact-producing agents. These perturbations or agents are associated with each subactivity (and in some cases structures resulting from subactivites) in a third matrix (Figure 6).

The Impact Matrix

Impacts from oil shale development can be traced by linking the perturbations and agents with key ecosystem components and processes in an impact matrix. For Tract C-b, this matrix arrays 79 rows of processes and components against 71 columns of driving variables, oil shale perturbations and agents, and state variables that interact with the row components and processes. Each of the 5,609 cells was evaluated to determine whether there could be an effect, and if so, whether it was direct, indirect, or both.

Diagrams of the Tract C-b Ecosystem

Three different types of diagrams were used to depict the Tract C-b ecosystem conceptually: flow diagrams, system diagrams, and process diagrams. Flow diagrams were used to illustrate the flows of the various currencies among ecosystem components (Figure 1).

Two major system diagrams were drawn, one for the terrestrial portion of the ecosystem, and one of the aquatic portion. Each of these diagrammed the currency flows within each subsystem and linked all subsystems together with information linkages, as partly illustrated in Figure 2.

Process diagrams focus on the major influences that affect each important ecosystem process. These summarize not only the observed time dynamics of the donor and receiver state variables, but also on the dynamics of all the variables, state and driving, that affect the rate of transfer between donor and receiver. Process diagrams were drawn for each of the 85 processes included in the Tract C-b model.

In the example, Figure 7, the process of terrestrial animal emigration from the tract (FTEMI) is controlled by four driving variables (represented by pentagons at the top of the page) and two state variables (the rectangles at the bottom). The currency flowing from PTA, the population of terrestrial animals, into the sink (conceptually outside the system), is animal numbers.

ACTIVE ENVIRONMENTAL PERTURBATIONS	SUBACTIVITIES																	STRUCTURES									
	Disturb Vegetation	Remove Vegetation	Operate Equipment	Drill and Blast	Excavate and Fill (grade)	Dispose of Solid Waste	Pave or Surface	Fence	Increase Traffic	Remove Underground Water	Dispose of Process and Mined Dewatering Water	Sink Shafts	Build Conveyor	Operate Conveyor	Crush Mined Shale	Erect Structures (buildings)	Exhaust Returning Gases	Shafts	Roads and Paved Surfaces	Unpaved Roads	Fences, Culverts, and Other Barriers	Impoundments	Transmission Lines	Pipelines	Buildings	Underground Mines	Land Fills
METEOROLOGICAL																											
Create Fugitive Dust	●	●	●	●	●	●	●	●	●			●	●	●	●					●							●
Create Odors			●						●		●						●										●
Create Noise and Vibration			●	●		●			●				●	●	●	●											
Emit Steam																	●										
Create Water Vapor																											
Create Icing																	●										
Create Fog																	●										
Emit Particulates and Aerosols				●					●						●		●										
Emit SO_2																	●										
Emit H_2S																	●										
Emit NO																	●										
Emit NO_2																	●										
Emit NO_x			●						●								●										
Emit CO			●						●								●										
Emit CH_4																	●										
Emit NMHC (nonmethane hydrocarbons)																	●										
Emit THC (total hydrocarbons)			●						●								●										
Emit Ozone and Other Oxidants																	●										
Emit Arsenic																	●										
Emit Mercury																	●										
Emit Selenium																	●										
HYDROLOGICAL																											
Alter Surface Runoff	●	●			●		●				●					●			●	●	●				●		●
Alter Peak Flows (flash flooding)	●	●			●		●									●			●	●					●		●
Alter Sedimentation	●	●			●						●									●							●
Alter Evaporation											●								●			●			●		
Alter Seepage					●						●											●					
Alter Water Table Levels					●					●	●	●							●			●				●	
Alter Downstream Flow	●	●			●		●			●	●					●			●	●					●		●
Alter Stream Channels					●					●																	
Alter Surface Chemical Composition						●				●	●						●										●
Alter Groundwater Chemical Composition						●				●	●																●
Alter Groundwater Flow Systems				●	●					●		●						●								●	
TOPOGRAPHIC																											
Create Landslides	●	●		●	●		●					●							●	●						●	●
Alter Contour of Land					●		●												●	●							●
Alter Surface Drainage Patterns					●							●						●								●	●
EDAPHIC																											
Create Compaction			●		●		●		●				●			●											
Create Erosion	●	●	●		●	●					●		●			●				●							●
Remove All Vegetation		▼			●																						
Alter Humus Content	●	●	●		●	●																					
Mix Soil Profile				●	●	●																					
GEOLOGIC																											
Cause Ground to Subside				●	●							●						●								●	
Expose Shrink/Swell Clays				●	●													●								●	
BIOLOGICAL																											
Disturb Vegetation	▼		●																								
Increase Road Kills																			●	●							

● = These perturbations are identified as being associated with the corresponding activities and structures.

▼ = These can be considered either subactivities or perturbations.

Figure 6. Perturbation matrix. Environmental perturbations generated by associated oil shale development activities.[1]

Emigration, Terrestrial (FTEMI)

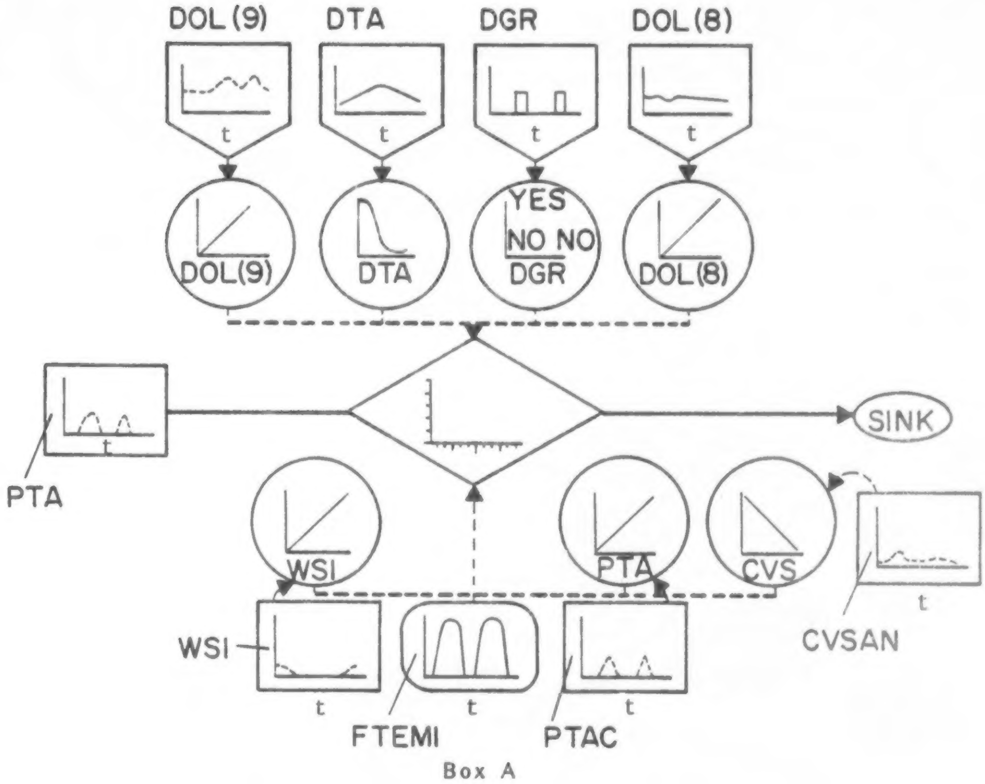


Figure 7. One of the 85 process diagrams used in the Tract C-b conceptual model. The process, emigration, is represented by the center diamond. Emigration controls the flow of animal numbers out of the system. Normal emigration rates are graphed in Box A. These rates are influenced by driving variables (the pentagons at the top of the page) and state variables (rectangles at the bottom). Circles represent the functional responses of emigration to the various state and driving variables. See text for discussion of nomenclature.[1]

The rectangle with rounded corners (FTEMI) at the bottom center of the figure represents the normal pattern of animal emigration. This pattern is influenced by the driving and state variables qualitatively as shown in the circles.

For example, the air temperature (DTA) changes seasonally, as shown in the pentagon. The influence of that seasonal temperature change is negatively sigmoid: i.e., as air temperature increases, the animals slowly begin to leave more and more rapidly; finally, when most of the animals have left the area, the emigration rate slows down again.

One projected influence of oil shale development on emigration is shown in the pentagon labled DOL(9), which represents the secondary hunting and recreation pressures brought to the area by the oil shale development. The dotted curve represents only an estimate from sources outside the baseline study. The effect of increased hunting and recreation pressure is assumed to be positively linear, as shown in the circle. The effect of snow (WSI), a state variable, on emigration is likewise projected to affect emigration in a positive linear fashion.

THE CONCEPTUAL MODEL

The preceding section provides a short explanation of our methodology. This section summarizes the model in a brief overview, discusses the utility of the model, and provides a retrospect on the project.

Overview of the Model

The seven ERUs in the model (Table 1) are linked by many flows of material in and out. Movement of animals, water, and litter across boundaries couple the ERUs. In addition, the relative acreages of ERUs change according to how man manipulates the ecosystem: deforestation, rehabilitation, and flooding all alter the character of response units, and these processes are included in the model.

Biotic state variables are represented by five groups of terrestrial plants, (each with three functional groups of plant parts), ten groups of terrestrial animals (Table 4), litter, aquatic vertebrates and invertebrates, rooted and nonrooted aquatic plants, and detritus.

Abiotic state variables include soil temperature, soil moisture, land surface area, water temperature, and water surface area. Fifteen driving variables were also included (Table 5). Flows among all variables are regulated by 85 processes in the model.

Observed behavior of many state and driving variables is represented by nearly 500 time-series graphs plotted against a standard 2.5-year $\underline{X}$ axis. These graphs were used to represent the behavior of variables in the process diagrams (Figure 7) in order to infer qualitatively the behavior of a particular process as influenced by the time-dynamics of the variables.

TABLE 4. SUBDIVISION OF STATE VARIABLES USED IN THE CONCEPTUAL MODEL, WITH SUBSCRIPTS

The subscript I refers to the ecosystem response unit

Aggregated State Variable	Subscript J	Disaggregated Variables
Terrestrial animals numbers--PTA (I, J) Terrestrial animal weights--GTA (I, J)	1	Cattle
	2	Deer
	3	Insectivorous birds
	4	Omnivorous birds
	5	Carnivorous birds
	6	Mammalian predators
	7	Rabbits
	8	Rodents
	9	Reptiles
	10	Arthropods
Live shoots--CVS (I, J) Live roots-CVR (I, J) Standing dead--CVD (I, J)	1	Annual plants
	2	Perrenial graminoids
	3	Perennial forbs
	4	Shrubs
	5	Trees

TABLE 5. LIST OF DRIVING VARIABLES AND THEIR ACRONYMS

Number	Variable Name	Acronym
1	Precipitation	DPT
2	Air Temperature	DTA
3	Wind	DWD
4	Solar Radiation	DRD
5	Forest Cutting Schedule	DCT
6	Cattle Grazing Schedule	DGR
7	Sulfur Compound Emissions	DOL (1)
8	Nitrogen Compound Emissions	DOL (2)
9	Ozone and Oxidant Emissions	DOL (3)
10	Trace Metal Emissions	DOL (4)
11	Carbon Monoxide Emissions	DOL (5)
12	Water Vapor Emissions	DOL (6)
13	Fugitive Dust	DOL (7)
14	Noise and Activity Disturbance	DOL (8)
15	Secondary Hunting and Recreation	DOL (9)

The model did not attempt to develop functional mathematical forms for these graphs, nor to develop equations to describe the processes.

Utility of the Model

This conceptual model describes major interrelationships on Tract C-b from a systems perspective. These interrelationsips consist of innumerable feedback loops within and between the living and nonliving portions of the system. The model focuses on major feedback loops as they operate on Tract C-b.

Because field data collection was not well coordinated in time and space among disciplines in the baseline studies, there was virtually no attempt in most of the summary volumes to cross-correlate data on the different ecosystem variables that were measured. The conceptual model draws qualitative inferences from those data as well as from other ecological sources and principles outside the baseline study.

A systems approach exploits the organizational power associated with different types of model-building to array, analyze, and synthesize environmental data and information to improve our understanding of the ecosystem and our ability to predict what will happen to that system if stressed by human-controlled or natural influences.

The approach here was largely qualitative. The model comprises box-and-arrow diagrams, matrices, and verbal description of the important environmental interrelationships that exist on the tract. Although these conceptualizations describe the behavior of ecosystem components and processes primarily in terms of their qualities, this step is always a necessary preliminary to more rigorous quantitative analysis.

The conceptual model documented in Van Dyne and Haug[1] serves several purposes.

- It pulls together a vast amount of information and data about Tract C-b within a logical conceptual framework.
- It summarizes most baseline information in nearly 500 time-series graphs that depict behavior of many components and processes in the ecosystem over a 2.5-year period.
- It serves as a cross-reference to data reported in earlier volumes of the report, via the time-series graphs.
- It points out deficiencies in the baseline study and identified gaps in the data.
- It provides a theoretical foundation from which a computer simulation model could be derived in the future.

- It permits users to track potential impacts qualitatively through the system.
- It assisted users in planning a monitoring program.
- It provides a tool for planning mitigation measures by identifying ways in which environmental perturbations or agents from oil shale development could move through the system and impact components removed in time and space.

Retrospect

The results of this modeling effort were both gratifying and frustrating. They were gratifying in that the modeling process enabled us to organize, classify, summarize, integrate, and synthesize the environmental baseline data into a crude first cut at understanding the ecosystem and the potential influences of oil shale development.

The exercise was frustrating for several reasons. First, having gone this far, we wish we could have taken the next step and developed the model into a full-blown simulation tool that could have been linked directly to monitoring and mitigation during the life of the project. Such a model very likely would have permitted the operator ultimately to reduce his monitoring program through a long range feedback-and-adjustment process.

By this is meant, as the model is fine-tuned using data from a long term monitoring program, critical ecosystem parameters (i.e., variables or processes) would have gradually been identified. The monitoring program could then have relied on measuring only those sensitive parameters instead of monitoring many parameters in the hopes that the sensitive ones were included. In other words, as our understanding of the ecosystem increased, as evidenced by the predictive capabilities of the model, unnecessary monitoring could have been phased out.

A second source of frustration was the lack of relevant data from the 2.5-year baseline study. After synthesizing nearly 500 time-series graphs from the baseline data, and after developing a conceptual ecosystem model, we found that any relationship between what was actually measured, and what should have been measured, was almost coincidental.

For example, man's influence on the ecosystem was virtually ignored. No information was available on hunting, recreation, forest cutting, and cattle grazing activities on the tract, although all four activities are known to occur. Environmental noise above background was measured, but there are no indications of what the source of that noise was. Although there are 42 time-series graphs dealing with birds, not one is available for deer numbers on the tract. Although cattle are known to graze the site, no figures were reported. A great quantity of water chemistry data was obtained, but they provide little relevant information.

Most of the items measured were variables. Little information was provided on process rates. No information was developed for factors influencing processes. Had the conceptual modeling activity been completed first, many of these information needs would have been identified, and baseline studies could have been more efficient, more focused, and better coordinated.

ACKNOWLEDGEMENTS

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GROUNDWATER QUALITY SAMPLING APPROACHES FOR MONITORING OIL SHALE DEVELOPMENT

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ABSTRACT

The development of cost-effective groundwater quality monitoring programs for oil shale development requires a structured (or planned) assessment process leading to selection of sampling sites and sampling methods. General Electric Company-TEMPO is conducting a study to assess the impacts of oil shale development on groundwater quality and to develop monitoring design guidelines. One of the roles of a structured design methodology is to assure the quality of monitoring data. This is accomplished by defining monitoring goals, evaluating monitoring options, and creating a framework for assessing cost-effectiveness. The groundwater quality monitoring design process includes:

- identification and characterization of potential sources of groundwater quality impact
- characterization of the location of these sources with regard to hydrogeology and existing groundwater quality
- assessment of mobility and attenuation of potential pollutants in the subsurface
- development of a priority ranking of potential sources of impact and of potential pollutants.

The purpose of utilizing such a monitoring design process is the collection of useful data. Design of groundwater quality data collection programs in the oil shale region poses some interesting problems as a result of the complexity of the hydrogeology of this area. Some of the key issues in selection of methods for sampling in the subsurface are:

- well completion
- use of pumping, bailing, or other techniques for sampling wells
- sampling frequency.

This paper outlines these considerations for selection of sampling approaches.

INTRODUCTION

The focus of this symposium is on sampling methods, analytical approaches, and quality assurance, in general, as related to oil shale development. Some of the analytical needs for environmental monitoring of oil shale operations are probably unique to this new industry. Monitoring of groundwater quality also presents some special requirements with regard to design of monitoring programs and selection of sampling methods. This is because of the hydrogeologic character of the oil shale region and because of the nature of some of the proposed development technologies (e.g., true and modified _in situ_ retorting). The keynotes of this paper are: (1) the need for _preplanning_ or structured design of data collection programs (data need a defined end use, as data have little intrinsic value), and (2) the role of sampling design in determining what is observed and the uses of groundwater quality data.

MONITORING PROGRAM DESIGN

General Electric Company-TEMPO is presently conducting a study concerning design of groundwater quality monitoring programs for oil shale development. This program, which is being conducted for the U.S. Environmental Protection Agency, includes consideration of deep mine-surface retorting operations such as proposed for Federal Lease Tracts U-a and U-b in Utah, and modified _in situ_ operations such as proposed for Tracts C-a and C-b in Colorado. The work scope of this effort is based on a general monitoring methodology developed by TEMPO (Todd et al.[1]) and includes the following sequence of steps:

- identify potential sources or causes of impact on groundwater quality and the potential pollutants associated with these sources

- carefully examine and interpret background data on the subsurface flow regime

- evaluate the mobility of pollutants in the subsurface

- develop a priority ranking of potential pollution sources and their associated pollutants based on: (1) mass of waste, concentration, persistence, toxicity, (2) potential mobility, and (3) known or anticipated harm to water users

- assess gaps in existing groundwater quality monitoring programs and design a monitoring program based on these gaps and the priority ranking.

Preliminary results of this study, including a preliminary priority ranking and monitoring program designs, are contained in a series of project reports (Slawson;[2] [3] Slawson and Yen[4]) and will not be presented in detail here.

The planning or structuring of the design of monitoring programs is essential to assure the quality of the results of that monitoring program. There are several avenues by which a structured design methodology, such as outlined above, provides this desired element of quality assurance.

First of all, such a methodology forces one to define that which is desired of the data collection program. By linking the processes of data collection and data assessment in the stepwise sequence outlined above, basic definitions of the use to which the data are to be put are provided prior to data collection. The data collection program is thus not developed in a vacuum with no predetermined data analysis-data use program.

Secondly, because the end uses of data are predetermined, the structured design methodology provides for evaluation of options, such as alternative sampling sites, sampling methods, sampling frequency, analytical methods, and other elements of the monitoring design. The basic technical rationale for selection among alternatives follows from consideration of which options provide the best (or at least adequate) data to address the defined needs (uses).

Related to these items is the development of cost-effectiveness criteria. The need for good, defensible data is undeniable, but recognition of economic realities, along with technical-scientific limits, is also necessary. A logical planning sequence can provide this desirable quality of cost-effectiveness to the monitoring design process as well as to the monitoring design itself.

GROUNDWATER SAMPLING METHODS

The methodology described above provides a logical framework for design of groundwater quality monitoring programs, including selection of sampling sites, well construction features, sample collection methods, and sampling frequency. In the oil shale regions, the complexity of the hydrogeologic systems encountered can present some special problems with regard to these monitoring components. The influence of the hydrogeology of the oil shale region on these considerations is the topic of the following discussions.

Sampling Sites

Groundwater flow in the Piceance Creek Basin occurs in several complex systems of fractures and faults. The evaluation of a fractured-rock flow system is generally much more complicated than assessment of a granular, porous media type of aquifer system. In fractured-rock systems, even defining the direction of flow may not be straightforward. Generally, the direction of flow and the flow gradient in groundwater systems are identified by measuring the head (or water level) in a set of wells and estimating lines of equal head. Flow then is perpendicular to these equipotential lines

(Figure 1). However, flow in fractured rock is along fractures and these flow paths can provide a flow direction which is nearly perpendicular to that which may be estimated from simple observation of head levels (Figure 2). Using this illustration (Figure 2), placing a well at point B to monitor the effects of an injection well or other waste source at point A would clearly not produce data which address the defined information requirements. The need for detailed hydrogeologic evaluation is thus an integral part of the monitoring design methodology.

Well Construction

The aquifer systems in the Piceance Basin include a series of horizontal fracture sets very irregularly interconnected by vertical fractures and faults. The system has commonly been portrayed as including two aquifers separated by the rich oil shale beds of the Mahogany Zone. In actuality, the irregular spacing of both vertical and horizontal fractures, the appreciable variability of hydraulic properties among these fracture sets, and the varying degrees to which halite and nahcolite minerals have been leached from different zones, create numerous distinct aquifer units. Where wells are located and where they are perforated (open to water-bearing zones) have a significant influence on the data collected. This is true for data on both aquifer characteristics and groundwater quality.

Consider, for example, two wells located close together and which are perforated over exactly the same interval. The perforated interval contains two fractured strata of equal hydraulic conductivity (Figure 3). One strata contains abundant saline minerals and the other little. One well intersects a fracture in the upper strata, but none in the lower (saline) strata, while the other intersects a fracture in only the lower strata. These two wells will provide drastically different water quality data in spite of their proximity and construction similarity.

This situation may be further complicated by varying permeabilities of different strata. Some fine-grained, high-organic level strata are resistant to fracturing and may form effective aquitards. This can result in different head levels between layers and mixing of highly different quality waters in interconnections, such as well bores. As an example of how well completion (and recompletion) can affect water quality data, consider the following data reported for Tract C-b (C-b Shale Oil Venture[6]).

Original Well Designation	TDS before Recompletion	TDS after Recompletion	New Well Designation
SG-11, string 1	39,000	16,000	SG-11, string 1R
SG-10	42,000	2,800	SG-10R
SG-17, string 1	28,000	4,300	SG-17, string 1R

These wells had initially encountered and been open to a highly saline water zone which apparently had a higher hydrostatic head than less saline overlying aquifer zones. Thus water collected from these overlying zones was affected by the interconnection. Recompletions were undertaken to isolate these different water quality zones.

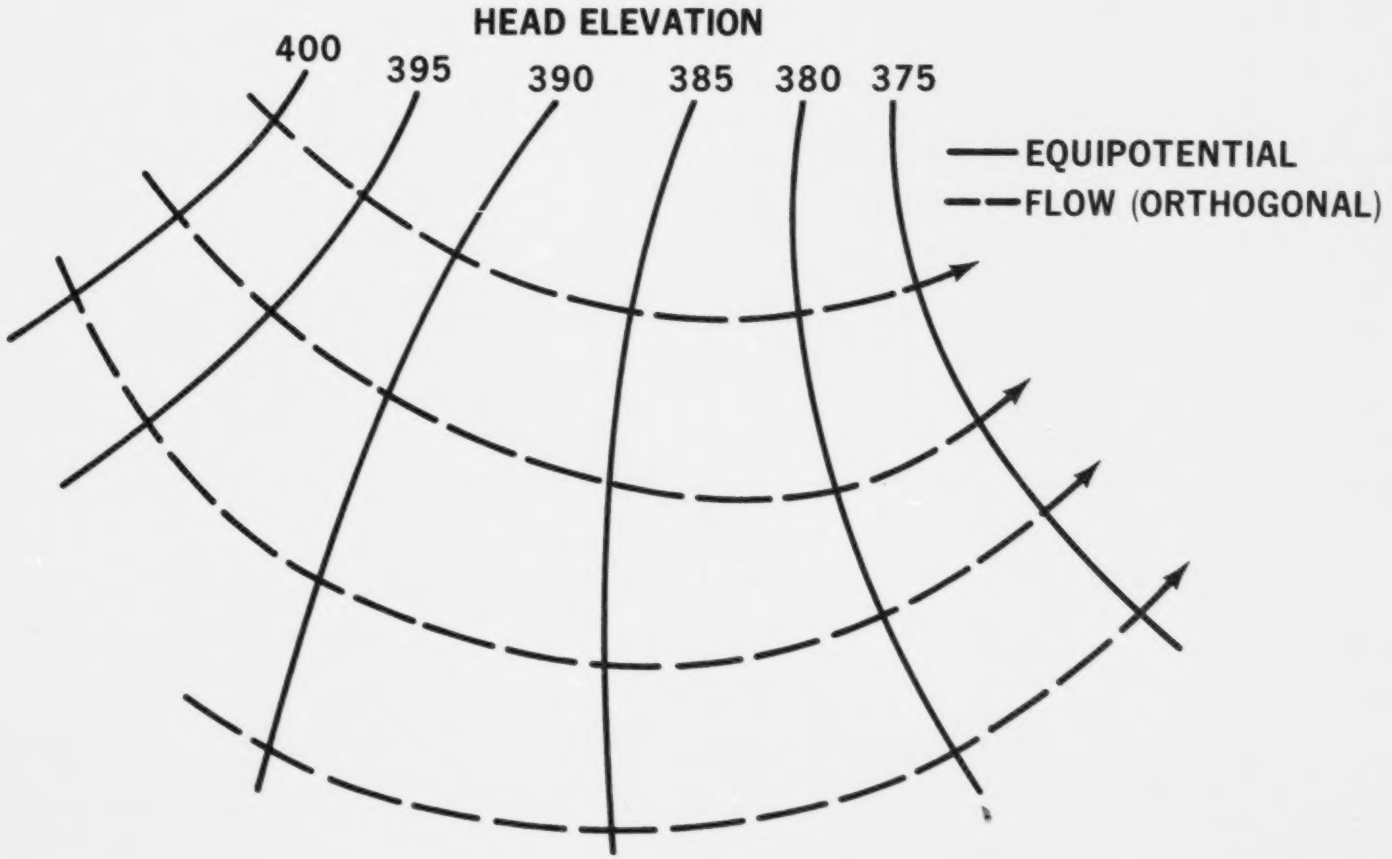

Figure 1. Sample of groundwater flow net.

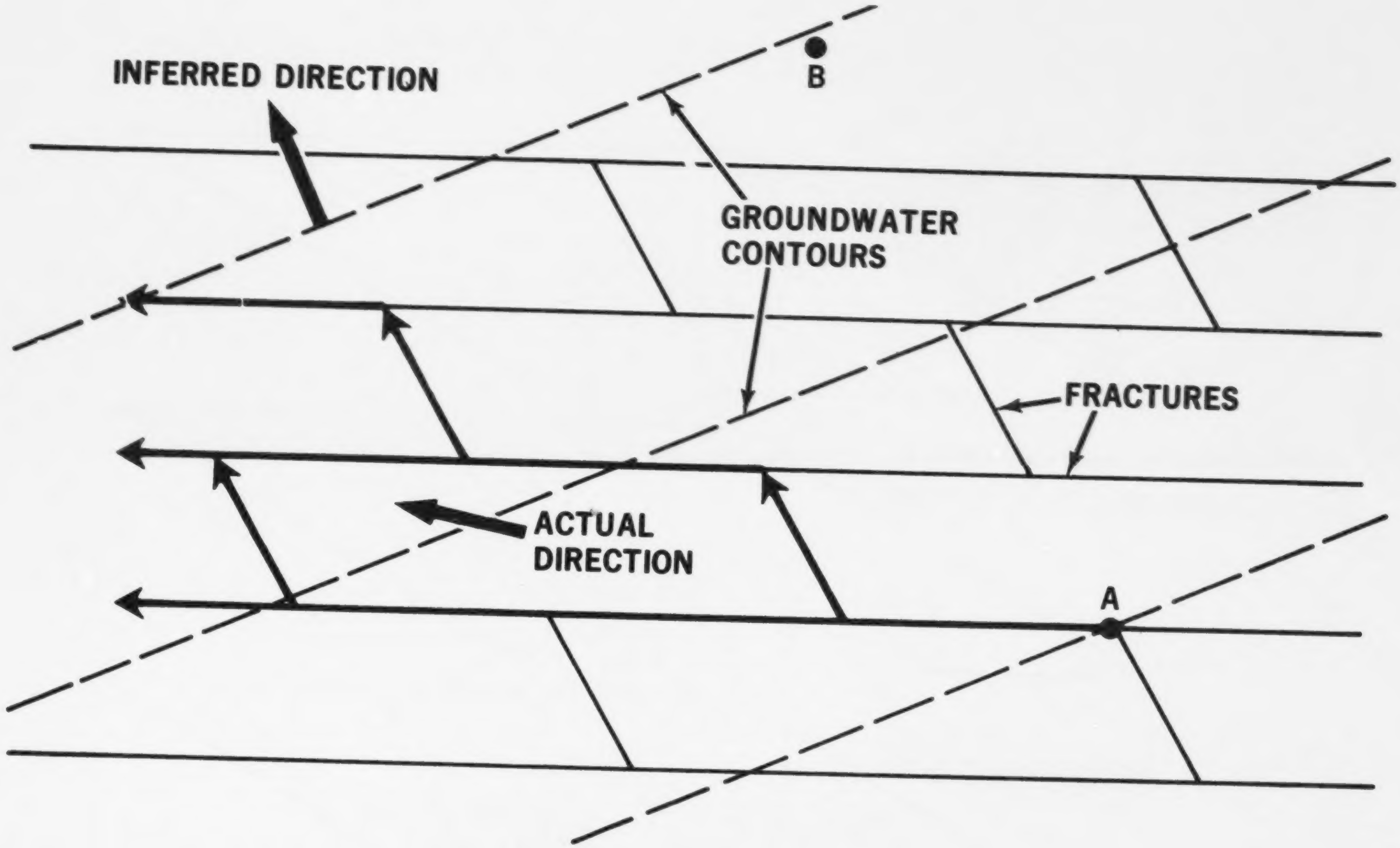

Figure 2. Idealized two-dimensional pattern showing the relation between true direction of groundwater flow and the direction inferred by drawing orthogonal lines to the regional water level contours (adapted from Davis and DeWiest[5]).

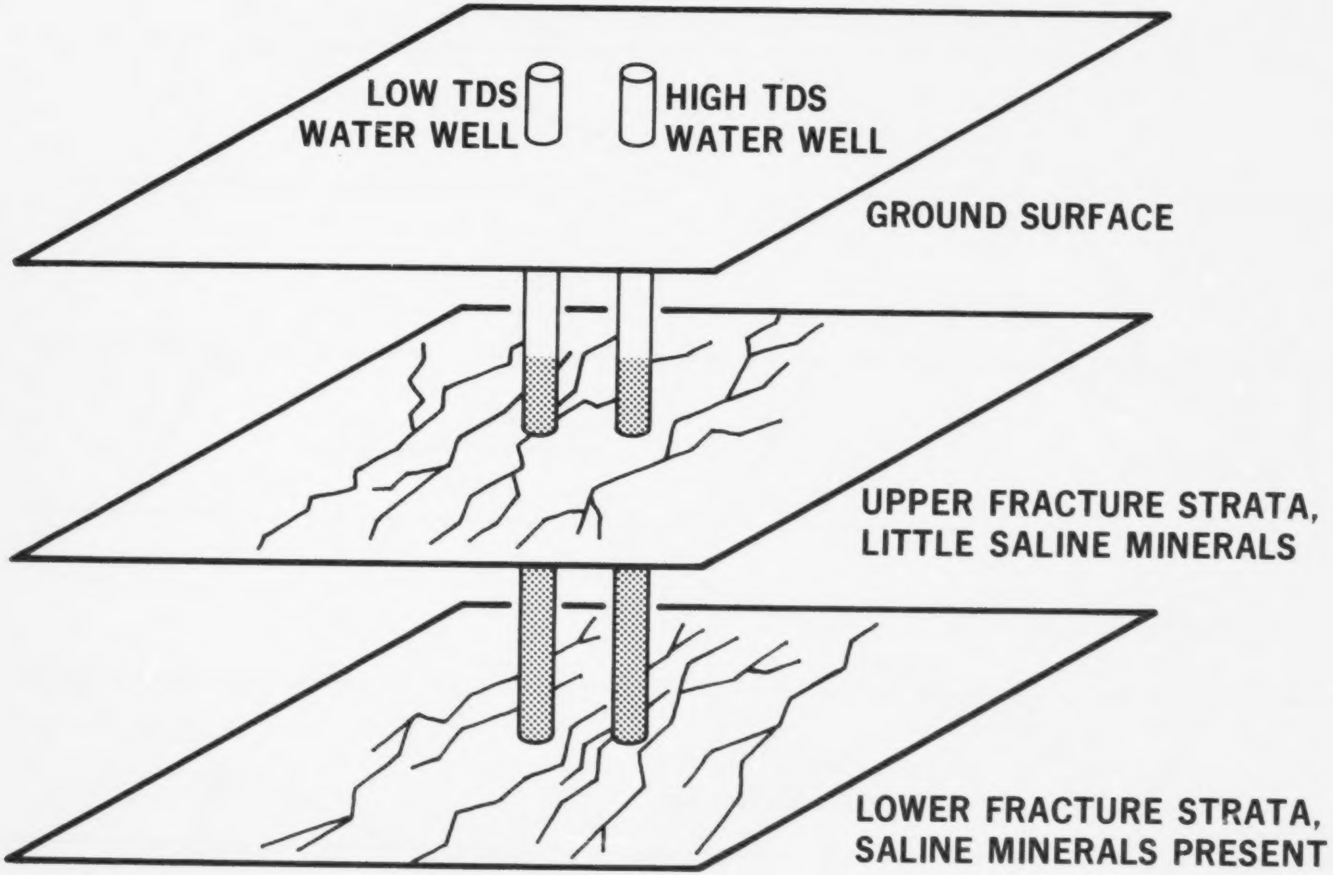

Figure 3. Fractured-rock aquifer system yielding water of varying quality depending on location and perforation of wells.

Also, interval of completion and perforation may affect water level data. For example, on Tract C-b, an apparent mound of water in the center of the tract may be due to data from a well (SG-6) completed over a small segment of the aquifer zone. If this interval has a high head, then this well will show a greater head level than other wells in the area which are perforated over a wider zone and thus exhibit a more average head.

Sample Collection Methods

Methods currently being used to collect groundwater samples on the oil shale tracts include bailing, swabbing, and pumping. The choice of sampling method can greatly influence the results of water quality sampling and thus the interpretation of monitoring data.

On Tract C-a, all groundwater quality samples are collected by bailing. Sufficient water is bailed to fill the required sample bottles. One of the goals of sampling is to obtain water quality data which are representative of water within the aquifer zone being sampled. Aside from problems of well completion, bailing of a small volume from a well bore may not provide the desired representative sample. For example, construction of deep wells may include a perforated zone of perhaps 300 feet (91 meters). A 6-inch (15-centimeter) casing 300 feet long contains about 450 gallons (1,700 liters) of water. If approximately 4 gallons (15 liters) is bailed for sampling, for example, on a quarterly basis, water sampled may not be representative of local groundwater, but water which has been standing in the well bore (perhaps a very different physiochemical environment) for some time.

The implication here is that care must be taken with the use of bailing as a sampling technique. For example, tests conducted by Rio Blanco Oil Shale Project (Tract C-a) indicated that samples bailed from well intervals perforated in aquifer zones produced results very comparable to pumped water samples. However, samples bailed from the well interval above the perforated zone (and where water is stagnant within the well) yielded water quality data quite different from either pumped samples or samples bailed from the aquifer zone.

Swabbing, which is used to collect samples from deep aquifers on Tract C-b, includes the use of oil field equipment to collect water samples. Several swabbing runs, removing the water column from the well bore, are made prior to collection of samples for laboratory analysis. This approach may provide water quality samples more representative of local aquifer conditions than bailing, as several well volumes are removed prior to actual sample collection.

Care must also be taken with the swabbing techniques so that contamination of samples (such as from organics from the oil field equipment) does not occur. In addition, the swabbing action may accelerate the plugging of well perforations by the action of the rubber swabbing cup on the casing. The amount of water swabbed from a well must be carefully considered to obtain consistent and representative samples. Variations in water quality (conductivity) observed during swabbing are shown in Table 1.

Table 1. RANGE OF CONDUCTIVITY OBSERVED AND FINAL CONDUCTIVITY LEVEL OF SWABBED SAMPLES, TRACT C-b, FALL 1976

Well/string number	Gallons swabbed	Observed conductivity range (μmhos/cm)	Final conductivity (μmhos/cm)
SG-1, #1	1,260	3,000 - 10,000	8,250
SG-1, #2	2,840	1,200 - 1,500	1,250
SG-9, #1	2,100	1,300 - 3,400	2,000
SG-9, #2	1,150	1,850 - 2,100	1,850
SG-21	3,210	750 - 1,150	1,000
Cb-4	2,300	800 - 900	825
SG-11, #12	1,220	14,000 - 32,000	22,000
SG-11, #2	530	800 - 4,000	1,200
SG-11, #3	300	1,600 - 1,800	1,790
SG-18A	--	750 - 1,250	1,000
Cb-2	2,920	1,600 - 1,650	1,600
SG-6, #1	550	1,800 - 3,100	3,000
SG-6, #2	630	1,300 - 1,400	1,300
SG-6, #3	160	1,350 - 1,550	1,550

Many of the difficulties of obtaining representative samples by bailing or swabbing are overcome by use of a submersible pump to collect samples. By pumping, a relatively large area of the aquifer is sampled rather than a zone within or immediately adjacent to the well bore. This "sampled zone size" is an important consideration for monitoring purposes, as well as for general collection of representative samples. For example, assume a well is perforated throughout the water-bearing zone (Figure 4). Bailing will sample essentially the width of the well bore, perhaps 6 or 8 inches of the aquifer cross section. Swabbing would sample a wider cross section (perhaps several tens of feet). Obviously, the opportunity of detecting the mobility of potential pollutants is enhanced by sampling a greater cross section of the aquifer.

Care must also be taken in the design of sampling programs which include pumping. As shown in Table 2, water quality can vary greatly as pumping continues. A schedule of pumping time before sample collection has to be established, largely by trial sampling of each well and frequent sampling of, for example, conductivity and pH, in the field during pumping.

Sampling Frequency

Defining an appropriate sampling frequency is a complex issue influenced by location of sampling sites, monitoring goals, climatological factors, and characteristics of groundwater flow. As a result, sampling frequency should be defined on a case-by-case and likely trial-and-error basis. One of the key factors is groundwater flow rate. If flow from a potential pollution source to a monitoring well is expected to be on the order of decades (assuming a release occurs), then very frequent sampling does not seem warranted and perhaps annual sampling for a few indicator constituents would suffice.

The complexity of the hydrogeology of the oil shale region makes estimation of groundwater flow rate difficult at best and the actual flow rates highly site specific. Table 3 lists some estimates of travel time in the upper aquifer zone of the Piceance Creek Basin. The wide variation in results reinforces the care needed in design of monitoring programs, as our understanding of the system is incomplete.

CONCLUSION

The goal of monitoring programs is to gather information, such as water quality data, for some decisionmaking process, such as determining the effectiveness of environmental control or mitigation measures. The quality of the data obviously influences the quality of the decision. The assurance of quality data comes from the planning and structured design of monitoring programs as much as from the use of reference samples, spiked samples, duplicate or repeat samples, standard analytical methods, proper instrument calibration, chain-of-custody procedures, and the other activities more normally associated with quality control-quality assurance programs. Without such planning, one may collect very "good" data which are inadequate in some way for the decisionmaking process.

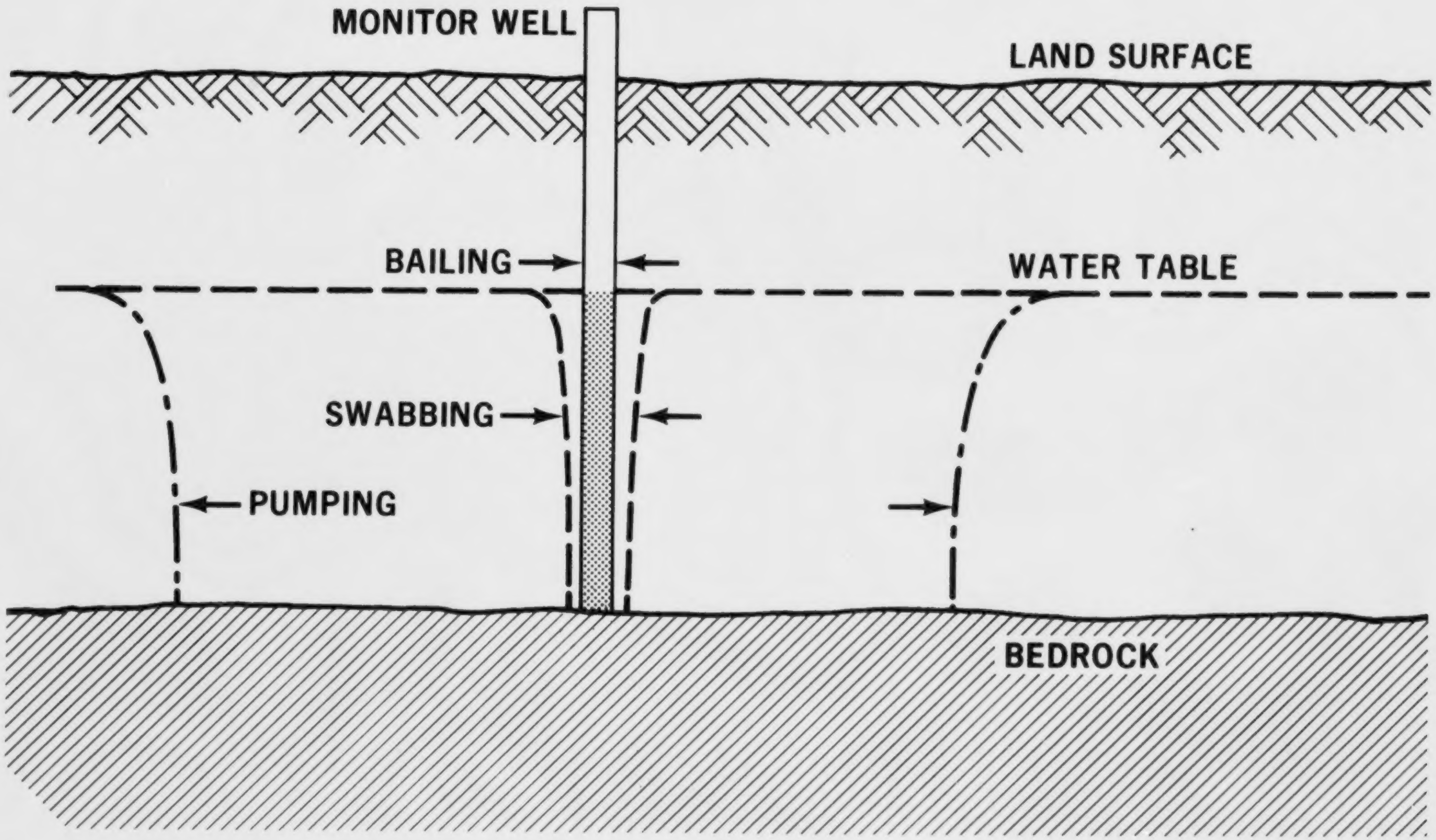

Figure 4. Schematic of size of aquifer cross section sampled by bailing, by swabbing, and by pumping of monitor well.

TABLE 2. FLUORIDE AND BORON FROM LOWER AQUIFER PUMP TEST
(C-b Shale Oil Venture[6])

Date (1975)	Fluoride (ppm)	Boron (ppm)
January 20	18.0	0.65
February 5	18.1	0.88
February 23	20.0	1.15
February 24	20.1	1.10
February 25	20.4	1.13
February 27	18.4	1.2
February 28	20.4	1.6
March 1	20.2	1.42
March 3	19.0	2.58
March 5	20.0	2.02
March 7	21.2	2.18
March 19	23.2	2.00

TABLE 3. FLOW RATES OF THE UPPER AQUIFER, PICEANCE CREEK BASIN, ESTIMATED BY THREE STUDIES

Study Reference	Flow Velocity (feet per day)	Travel Time (years to travel 1 mile)
Lawrence Berkeley Labs, 1978[7] (data from Weeks et al., 1974)[8]	0.05	300
U.S. Atomic Energy Commission, 1972[9]	0.36-0.78[a]	20-40
Knutson, 1973[10]	11-7	1.2

[a] Range for representative gradient and maximum gradient cases.

Some of the analytical needs for environmental monitoring of oil shale operations are probably unique to this new industry. Monitoring of groundwater quality also presents some special problems with regard to selection of sampling sites, well construction, sample collection methods, and sampling frequency. This is because of the complexity and heterogeneity of fractured rock and/or solution cavity aquifer systems, such as are found in the oil shale region. Special care must be exercised in sampling in such hydrogeologic systems to assure that what is being sampled is that which one desires to sample and also that which one thinks is being sampled.

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QUALITY ASSURANCE FOR WATER MONITORING PROGRAMS

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ABSTRACT

The primary objective of quality assurance is to insure that generated data are complete, accurate, representative and legally defensible. Consequently, the development and implementation of an effective quality assurance program is an integral part of operating a reliable water monitoring program.

Although a major portion of the quality assurance effort is normally expended in the laboratory, quality assurance activities associated with field sampling and data handling must also be addressed to insure that the integrity of the data is maintained from the time the sampling network is designed until the data are made available to the data users. An overview of these major internal and external quality assurance considerations for field sampling, laboratory analysis and data handling will be discussed. Review will also be made of neglected aspects of quality assurance such as: management overview of quality assurance activities; management commitment of resources to establish and maintain a quality assurance program; establishment of acceptance/rejection criteria used to maintain system control; initiation of appropriate corrective action; and, providing indicators of data quality to data users.

In addition, information will be provided to interested conference participants for obtaining EPA audit samples, manuals, and guidance documents associated with quality assurance.

(Paper presented at Symposium but not submitted for publication in the Proceedings. For more information, contact the author.)

QUALITY ASSURANCE IN SAMPLING AND ANALYSIS OF OIL SHALE RETORTING OPERATIONS

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Because of wide variations in oil shales, retorting processes, and operations of oil shale retorts, there is a need for a sound quality assurance program in sampling and analysis of oil shale retorting operations. Oil shale, its products, and its processes are unique--oil shale is similar to, yet differs from limestone; the retorting process is similar to, yet differs from coal liquefaction; crude shale oil is similar to, yet differs from conventional crude petroleum. Standard procedures for sampling and analysis of these more common materials and processes, when applied to oil shale retorting operations, often lead to erroneous and misleading results.

Any quality assurance program, in order to assure that its data are accurate and valid, needs the combination of the researcher and his array of analytical tools and the process operator and his knowledge of the process being evaluated. Because of the uniqueness of oil shale, its products, and its processes coupled with the variability of these facets, many samples which have been taken and analyzed are representative only of that sample.

RESULTS AND DISCUSSIONS

Raw Shale

Raw oil shale has been described as a solid hydrocarbon polymer cross linked with numerous sulfur, nitrogen and oxygen atoms embedded in a mixture of minerals. The richness, or grade, usually expressed in gal. oil/ton shale (or GPT) varies widely (0 to 80 GPT) in the Green River Formation. These variations have been shown to exhibit a correspondence between grade and particle size of crushed material. The higher the grade, the tougher the material and the larger the particle size.[1]

Raw shale, like limestone, when heated, produces lime. Yet raw shale, when subjected to higher heating or longer periods of heating, unlike limestone, loses the lime which had been formed.[2] This loss is caused by thermal reactions forming calcium silicates or aluminates.

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Finally, the trace metal constituents, important environmentally and in downstream refinery processing, vary quite widely with the location of the shale (see Table 1).[3]

Process

The products of oil shale retorting vary widely with the retorting process used to produce those products.[3] All products appear to vary widely in their chemical and physical properties. Crude shale oils, obtained from various processes, are shown to vary in their physical properties, such as pour points and their initial to 5 percent boiling range; and chemical composition, such as trace elements and special organic components such as paraffins, PAAH, and BaP (see Table 2). Note especially that no valid relationship appears to exist between weight percent benzene extractables and selected polyaromatic hydrocarbons such as benz-alpha-pyrene (BaP). Retorted shales also vary with the process. Data in Table 3 show differences in organic carbon, total carbon, and trace metals.

Operations

One operation for the Paraho retort is the Direct Mode where combustion of the carbon on the retorted shale serves as fuel for the process; combustion is done directly in the retort. Another mode of operation is the Indirect Mode where retorting is carried out by gases heated externally; combustion is done indirectly outside the retort. Data in Table 4 show some of the differences obtained for the product gas and retorted shale from the Paraho Direct and Indirect Modes of operation.[4] Gas from Direct Mode is diluted with nitrogen and carbon dioxide from internal combustion. That internal combustion also causes less organic carbon, LOI, and mineral.carbon on the Direct Mode retorted shale.

Others

Another product of oil shale retorting operations is process water. This water is produced primarily by combustion, moisture, mineral decomposition, and organic kerogen breakdown. It is swept from the retorting zone as a vapor with the oil, gases, and particulate fines and is condensed with the oil as a liquid. Water, because of its ubiquitous nature, the availability of many well-defined standard methods, and general ease of analysis has been sampled and analyzed frequently by many laboratories. As shown in Table 5, process water from oil shale retorting operations, in many cases, cannot be analyzed routinely by standard methods.[5] Chloride, determined titrimetrically with mercuric nitrate, will yield results in the order of 1 to 10 percent, or about tenfold higher than when titrated after interferences are removed by mild oxidation using HNO_3 boiling and acidification. Boiling is also required before the colorimetric determination of nitrate is performed. Nitrate results without pretreatment can be more than 10,000 times too high. The most common problem is in the determination of total dissolved solids. Ammonium salts, carbonates, and/or bicarbonates are the principal dissolved solids. Normal drying to 180°C results in losses due to volatilization of these ammonium salts. Speciation lends yet another problem. Errors in differentiating carbonate and bicarbonate in these complex waters are common. Problems with sulfur types--sulfate, sulfite, thiosulfate, and sulfide--have been identified and are being studied.[6]

CONCLUSIONS

In order to guard against erroneous conclusions drawn from the environmental analyses of oil shale retorting operations, a quality assurance (QA) program must be well planned.

The QA program needs--

- Cooperation between the researcher and the process operator to assure that raw shale samples are representative of the deposit and to assure that products are representative of the process.
- Careful examination of sampling and storage procedures and comparison of various analytical methods to be sure that the results are indicative of sample composition rather than the procedures and methods used.

In the Paraho Laboratory, a six-point QA program is used to evaluate data produced in the lab or submitted by various researches for review. This six-point QA program is outlined in Table 6. We have found it helpful in eliminating most of the eroneous data obtained from the characterization of oil shale retorting operations.

ACKNOWLEDGEMENT

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TABLE 1. COMPARISON OF RAW SHALES

Parameter	RS-101	RS-102	RS-103
Oil, gallons per ton	27.1	23.3	23.6
Carbon, wt.%	18.4	15.7	17.3
Mineral Carbon, wt.%	5.11	4.66	4.18
Sulfur, wt.%	0.62	0.69	0.24
Lead, ppm	16.00	20.00	15.00
Chromium, ppm	23.0	28.0	48.0
Zinc, ppm	80.0	102.0	82.0
Vanadium, ppm	73.0	84.0	97.0

TABLE 2. COMPARISON OF CRUDE SHALE OILS

Parameter	RO-1	RO-2	RO-3	RO-4
Viscosity (SUS 100°F)	174.2	125.7	131.6	107.2
Viscosity (SUS 210°F)	42.3	39.4	40.2	38.1
Pour Point, °F	+85.0	+80.0	+65.0	+70.0
Solvent Fractionation (Schwager and Yen)				
Oil, wt.%	85.1	90.3	87.4	81.3
Asphaltenes, wt.%	2.1	1.8	1.3	6.2
Resins, wt.%	12.8	7.9	11.3	12.6
Sulfur, wt.%	0.68	0.69	0.81	0.80
Nitrogen, wt.%	2.17	2.04	1.82	2.05
Polycyclic Aromatic Hydrocarbons (PAH)				
Benzo (a) pyrene (BaP)				
Parent, ppb	1800.0	1800.0	2300.0	4250.0
Polycyclic Aromatic Aza-hydrocarbons (PAAH)				
Acridine, ppb				
Run 1	20.0	< 20.0	< 20.0	< 20.0
Run 2	47.0	< 20.0	< 20.0	< 20.0
5% Boiling Range (°F)				
Initial	165.0	160.0	70.0	0.0
5%	375.0	375.0	325.0	250.0

Acridine was the only PAAH detected in the oil samples. The detection limit was 20 ppb.

TABLE 3. COMPARISON OF SPENT SHALES

Parameter	SS-201	SS-202	SS-203	SS-204
Loss on Ignition, wt.%	15.1	28.5	26.7	7.2
Carbon, wt.%	5.15	10.50	9.90	0.62
Mineral Carbon, wt.%	3.85	5.75	5.78	0.31
Organic Carbon, wt.%	1.30	4.75	4.12	0.31
Sulfur, wt.%	0.56	0.73	0.56	0.78
Lead, ppm	17.0	17.0	21.0	23.0
Chromium, ppm	37.0	46.0	31.0	37.0
Zinc, ppm	86.0	75.0	95.0	37.0
Vanadium, ppm	100.0	98.0	108.0	140.0
				137.0

TABLE 4. PRODUCT GAS COMPOSITION

	Direct Mode	Indirect Mode
Hydrogen, vol.%	4.6	24.8
Nitrogen	64.3	0.7
Oxygen	0.0	0.0
Carbon Monoxide	2.5	2.6
Methane	2.3	28.7
Carbon Dioxide	22.5	15.1
Ethylene	1.0	9.0
Ethane	0.6	6.9

RETORTED SHALE COMPOSITION

	Direct Mode	Indirect Mode
Ignition Loss, wt.%	17.72	23.32
Organic Carbon	1.97	3.06
Total Carbon	6.30	8.37
Mineral CO_2	15.86	19.47

TABLE 5. PROCESS WATER ANALYSIS

Parameters	Standard Method	Comments	Modified Method
Mineral Carbon	16.8 gm/l Total Carbon	Particle size is critical	3.54 gm/l
Chloride	No endpoint 25,329 mg/l	Organics present tend to precipitate the mercury as salts	3,400.0 mg/l
Nitrate	30,000 ppm Other labs 1 ppm	Carbonates and volatile organics must be removed	1.0 ppm
Phosphate	1-10 ppm Other labs 0.5 ppm	Color of solution interferes unless removed	0.5 ppm
Phenol	130 mg/l Other labs 8 ppm	Basic extractions and distillations must be done	8.0 mg/l
TDS	43.6 gm/l (anions + cations)	Drying conditions must be specified for continuity	119.4 gm/l

TABLE 6. QUALITY ASSURANCE PROCEDURES

1. Material Balance or Electroneutrality
2. Process Balance
3. Intralaboratory Comparisons
4. Standard (Spike) Addition
5. Analysis of a Standard
6. "Reasonableness"

USE OF ZEEMAN ATOMIC ABSORPTION SPECTROSCOPY FOR THE MEASUREMENT OF MERCURY IN OIL SHALE GASES

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Preliminary investigations of pilot-scale oil shale processing plants,[1,2] indicate that the level of mercury in offgasses may be significant. Extrapolation of these results to field conditions suggests that a 100,000 barrel per day oil shale plant processing 100 ℓ/tonne (24 gal/ton) oil shale with an average mercury content of 0.86 ppm[3] may release approximately 32,900 kg of mercury per year to the atmosphere. In contrast, the amount of mercury released from world coal consumption in 1967 is estimated to be 18,900 kg of mercury.[4,5] These data suggest that mercury emissions from oil shale plants may be of future environmental concern and that they may require control technology to reduce mercury levels. This will require reliable techniques to measure the mercury in these gases.

Reliable and representative measurements of mercury in gases from _in situ_ shale plants are difficult to obtain. Fox and others found that the mercury concentration in these gases may vary over several orders of magnitude.[1] Since retort runs may last many months, frequent sampling over a long time period must be employed to obtain representative mercury emission values. Conventional mercury gas stack sampling techniques such as gold bead absorption tubes or impinger trains are limited by interferences when applied to oil shale gases due to the presence of high concentrations of organic and sulfur compounds.

This paper describes a technique to continuously measure total mercury in the offgas from an oil shale plant or other similar plant on a real time basis. This technique utilizes Zeeman atomic absorption spectroscopy (ZAA) for the online measurement of mercury in the presence of smoke, organics and oil mist. The theory of Zeeman atomic absorption spectroscopy is presented along with a description of a new instrument suitable for use in field settings where wide temperature fluctuations may occur.

THEORY OF ZAA

Zeeman atomic absorption spectroscopy (ZAA) is an analytical technique similar to conventional atomic absorption spectroscopy (AA).[6,7,8] It differs principally in that the light source is placed in a magnetic field. This separates the original 2537 A resonance line into its linearly (π) and circularly (σ) polarized Zeeman components. The π component is used to

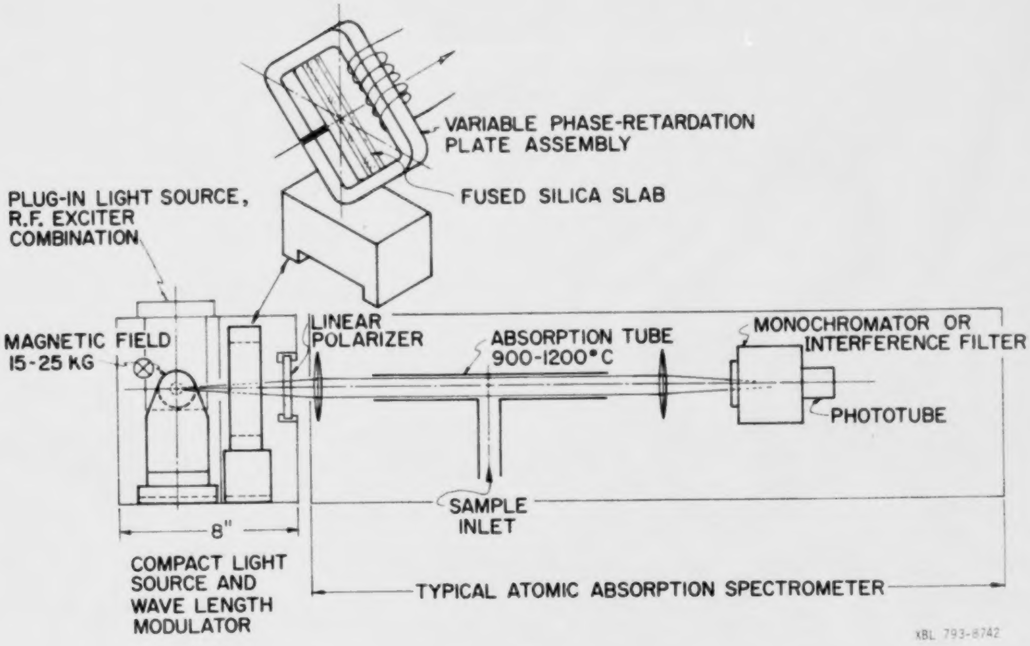
VARIABLE PHASE-RETARDATION PLATE ASSEMBLY
FUSED SILICA SLAB
PLUG-IN LIGHT SOURCE, R.F. EXCITER COMBINATION
MAGNETIC FIELD 15-25 KG
LINEAR POLARIZER
ABSORPTION TUBE 900-1200°C
MONOCHROMATOR OR INTERFERENCE FILTER
PHOTOTUBE
SAMPLE INLET
8"
COMPACT LIGHT SOURCE AND WAVE LENGTH MODULATOR
TYPICAL ATOMIC ABSORPTION SPECTROMETER
XBL 793-8742

Figure 1. Electro-optical components of a Zeeman atomic absorption spectrometer.[7]

detect the presence of mercury and the two σ components are used to monitor smoke and vapor in the light beam. A unique electro-optical switching device distinguishes between the π and σ components. These components are alternatively passed through the sample vapor and the difference in absorption of these two components is used as a measure of the amount of mercury present. Since the spatial and temporal variations in the π and σ components are identical, background correction capabilities are vastly superior to conventional AA techniques. Mercury can be measured in the presence of large quantities of smoke, organic molecules and other interfering substances.

A spectrometer consists of three major components (Figure 1): a light source which provides a 2537 A mercury emission line (π) and reference lines (σ) for background correction; a furnace-absorption tube assembly where vapors from thermally decomposed samples are swept into the light path of the emission and reference beams; and a detector which converts changes in the intensity of the transmitted probe and reference beams into an ac voltage for signal processing.

The key to the ZAA technique lies in the mode by which the emission and reference lines are generated and subsequently distinguished from one another. Both the emission and reference lines are supplied simultaneously by a single mercury discharge lamp operated in a 15 kG magnetic field. The Zeeman effect is the splitting of the original 2537 A emission line, in the

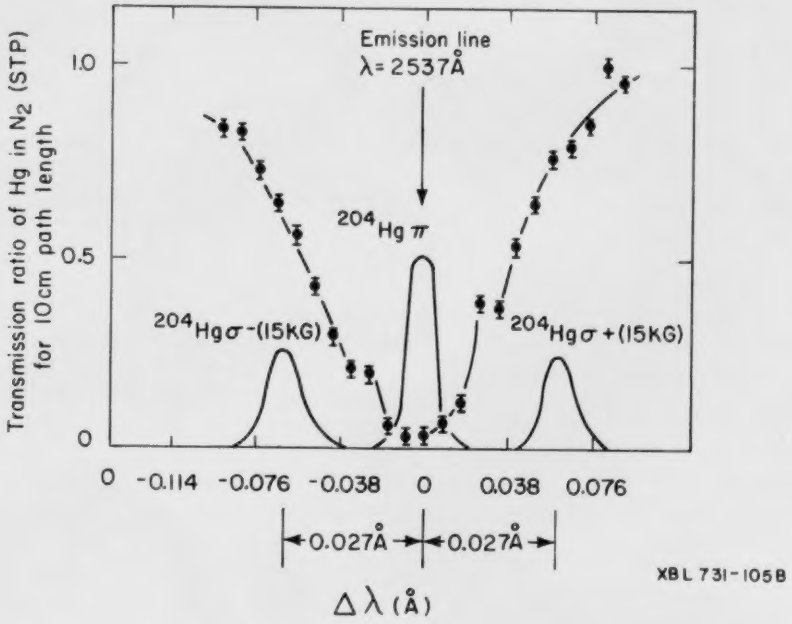

Figure 2. Comparison of the emission lines from a ^{204}Hg discharge lamp in a 15 kG magnetic field with the absorption profile (data points) of natural mercury at 1 atm of N_2.[8]

presence of a magnetic field, into its three Zeeman components: a σ- component shifted to a longer wavelength, a σ+ component shifted to a shorter wavelength and an unshifted π component. These Zeeman components for a ^{204}Hg lamp are shown in Figure 2.

The mercury present in the absorption tube consists of a naturally occurring mixture of several stable isotopes at a pressure of 1 atm. Thus the absorption lines of each isotope are pressure broadened. The resulting total absorption profile due to naturally occurring mercury (at 1 atm of N_2) is superimposed upon the Zeeman-split emission spectrum (Figure 2). Note that the π component coincides with the peak of the absorption profile for natural mercury, while the σ components are both on the outer edges of the profile. Therefore, the difference in absorption of the π and σ components may be used as a measure of the quantity of mercury present in the absorption tube. Here the π component becomes the probe beam and the σ components taken together become the reference beam.

The ZAA technique also provides a means of distinguishing between the π and σ components. When the light source is viewed perpendicular to the applied magnetic field, that is, along the optical axis of the instrument, both σ components are linearly polarized perpendicular to the field, while the π component is linearly polarized parallel to the field (Figures 1 and 3). Consequently, either component may be viewed independently of the other with a properly aligned linear polarizer.

Alternate selection of the π and σ components for detection before tansmission through the absorption region is achieved by using a variable phase retardation plate (VPRP) and a simple linear polarizer (Figures 1 and 3). The linear polarizer is oriented with its polarization axis parallel to the light source magnetic field (Figure 3). The VPRP (Figure 4) is a slab of fused quartz mounted inside a pulse-transformer core which has a driver coil on one side and a 0.5 mm air gap on the other. Varying the current through the driver coil applies a stress to the quartz plate. The stress axis of the quartz is oriented at an angle of 45° to the light source magnetic field.

The polarization axis of the incident linearly polarized light is rotated 90° as the light passes through the stressed quartz. This rotation is due to the difference in the propagation velocities for those components of polarized light which are parallel and perpendicular to the quartz stress axis. The amount of rotation is controlled by appropriate selection of current to the driver coil and the optical path length of the quartz. As seen in Figure 3, when the current applied to the driver coil is zero (no stress), only the π component is transmitted by the linear polarizer and thus passes through the absorption tube. When the driver coil current is adjusted so that the quartz is a half-wave plate (maximum stress), both π and σ components are rotated by 90°, and the linear polarizer passes only the σ or reference component.

The sample to be analyzed for mercury enters the furnace-absorption tube assembly where it is heated to 900°C. Mercury and its compounds atomize (thermally decompose) well below 900°C. Individual free atoms of mercury and decomposition products are then swept by the stream of sample gas into the light path of the absorption tube. Oxygen is introduced into the furnace chamber to promote combusiton of organics and thus reduce smoke. The π component is attenuated due to absorption by mercury atoms and scattering by decomposition products and smoke. The σ component is attenuated by scattering and smoke only.

The detector consists of an interference filter or monochrometer which passes all Zeeman components of the 2537 A line equally well, but blocks light of other wavelengths from striking the cathode of the photomultiplier tube (PMT). The PMT generates an output voltage proportional to the intensity of the π and σ components. If no mercury is present in the absorption tube, the probe and reference beams are absorbed and scattered identically by nonmercury background. Hence, as they alternatively fall upon the PMT, the light intensity does not change, and the PMT output voltage remains constant. In the presence of mercury, however, the probe component will be more strongly absorbed than the reference component, and the PMT output will vary at the audio frequency at which the switching from one beam to the other takes place (Figure 5).

The PMT output, together with an audio reference signal from the oscillator driving the magnetic clamp, is fed into the lock-in-amplifier (Figure 5). The tuned amplifier in the front end of the lock-in-amplifier accepts only those signals having the same frequency as that used by the VPRP to

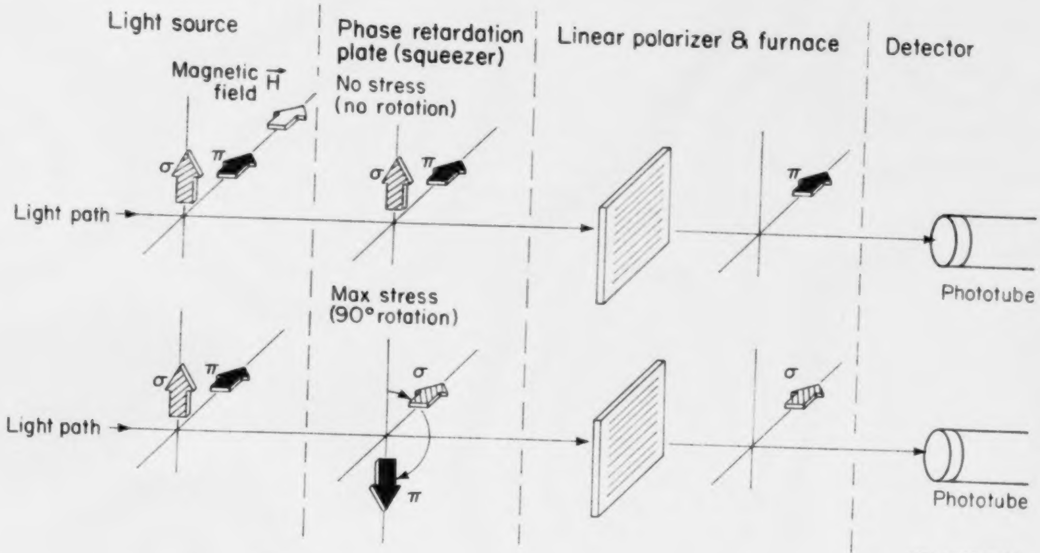

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Figure 3. Schematic Representation of ZAA Depicting π (probe) Beam and σ (reference) Beam Switching.

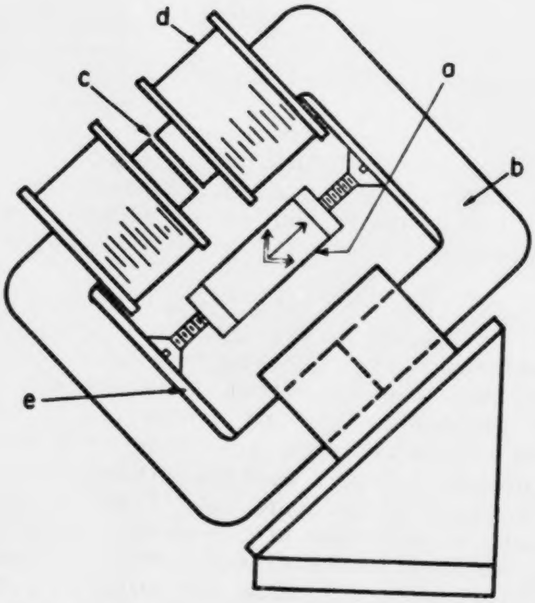

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Figure 4. Diagram of the current-controlled variable phase retardation plate. (a) Plate of fused quartz; (b) laminated pulse transformer core; (c) 0.5 mm gap; (d) drive coils; (e) stiffener plates. The long arrow in the center of the quartz represents the stress axis, while the double arrows depict the linear polarization axes of the π and σ beams.[6]

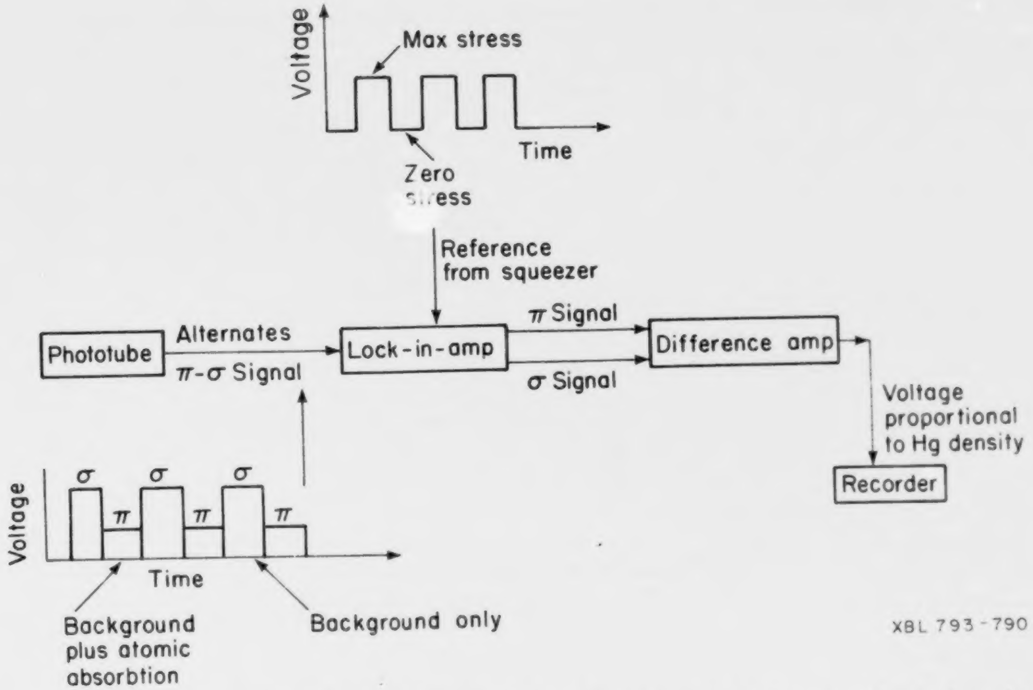

Figure 5. Signal processing electronics. To separate the π and σ signals, the lock-in amplifier requires a reference signal from the squeezer circuit. The square waves shown are an idealization; these signals actually vary sinusoidally.

switch between π and σ beams. This amplifier first recognizes and then takes the difference between the π and σ components in the audio portion of the PMT output. It supplies a dc voltage which is proportional to this difference and thus is proportional to the density of mercury in the absorption tube.

The accuracy of the background correction obtained by ZAA through the use of spatially and temporally coherent π and σ beams and synchronous beam switching and electronic signal processing techniques results in a significant advance beyond conventional AA background correction. As a result, ZAA is capable of performing accurately with up to 95% attenuation (from smoke or broad-band UV adsorption) of the π and σ components. Thus, ZAA is capable of direct analysis of most gas, liquid and solid samples for mercury without prior chemical treatment. This direct analysis capability is the major advantage of ZAA over conventional AA for online field measurements.

GAS MONITOR

A ZAA spectrometer has bee designed and built which is capable of continuously measuring mercury concentration in offgas streams on a real time basis. Specifically, a new light source, furnace assembly gas handling system and calibration system have been developed to accommodate gas

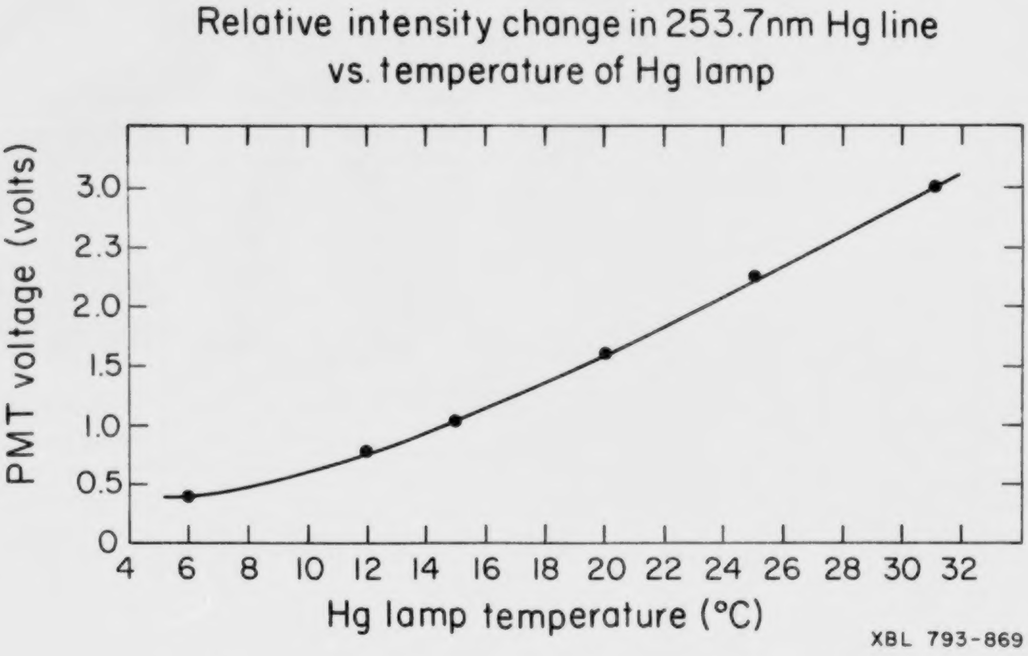

Figure 6. Change in the intensity of gaseous mercury discharge lamp with temperature.

sampling and mercury analysis under severe field conditions. These components and the performance of the instrument are described below.

Light Source

A new low-pressure mercury gaseous discharge lamp has been built and tested which will replace the radio-frequency excited electrodeless discharge lamp (EDL) previously in use.[6] This "pen light lamp" (PLL) consists of a U-shaped quartz tube containing argon and a small quantity of mercury. Minute electrodes are sealed in each end of the tube. The outer diameter of the tube is 7 mm. The lamp is surrounded by a soft iron water jacket fitted with a quartz window. The lamp-water jacket assembly fits between the pole tips of the permanent magnet which produces the Zeeman splitting of the resonance lines. The argon plasma and mercury resonance lines are produced by a 700 Hz high voltage driver. The 2537 A line intensity obtained with the PLL is approximately 50 percent greater than that obtained with the EDL.

By far the most temperature-sensitive component of the spectrometer is the light source. This represents a serious problem for field applications where significant temperature fluctuations are likely to occur. The variation in the intensity of the PLL 2537 A line with temperature is shown in Figure 6. From 12° to 31°C, the intensity increases by a factor of three due to an increase in the mercury vapor pressure within the lamp. However, over this temperature range the sensitivity or response of the ZAA to a

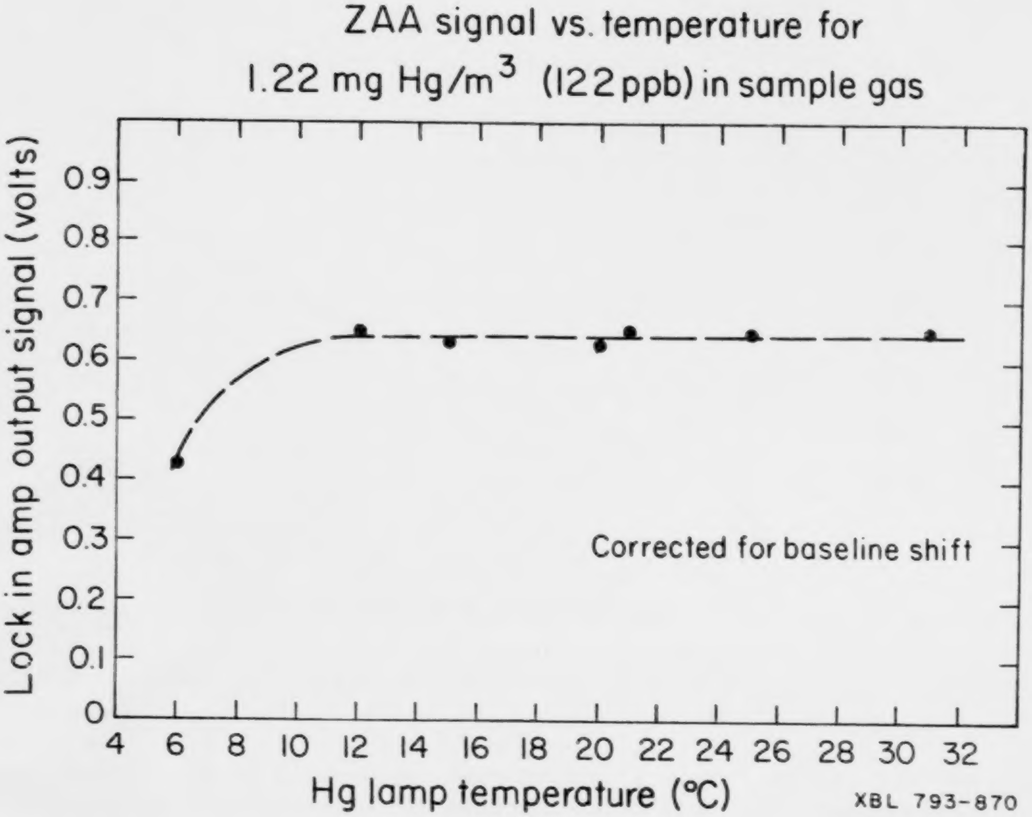

Figure 7. Temperature dependence of ZAA response to a constant concentration of mercury. The decrease in response at 6° C is an experimental anomaly caused by the defocusing of the light beam by water droplets condensed out on the outside of the light source window at this temperature.

constant concentration of mercury remains constant within measurement errors (Figure 7). This stability is achieved by routing the PMT signal through a log amplifier before it enters the tuned amplifier section of the lock-in-amplifier. Thus the electronic processing effectively filters out the effect of light intensity changes due to temperature fluctuations.

However, there is another temperature effect which is not filtered out by the electronics. The relative intensities of the π and σ lines are affected by self reversal or self-absorption of these lines within the plasma of the mercury discharge lamp. This self-reversal increases with temperature. This relative change in the π and σ intensities manifests itself as a change in instrumental baseline voltage and thus is indistinguishable from the signal produced by mercury in the sample gas. The magnitude of this effect is shown in Figure 8. In the absence of mercury a 12-31°C change in temperature produces a 220 mV ZAA voltage as shown by the lower curve in Figure 8. The upper curve shows this change in parts per

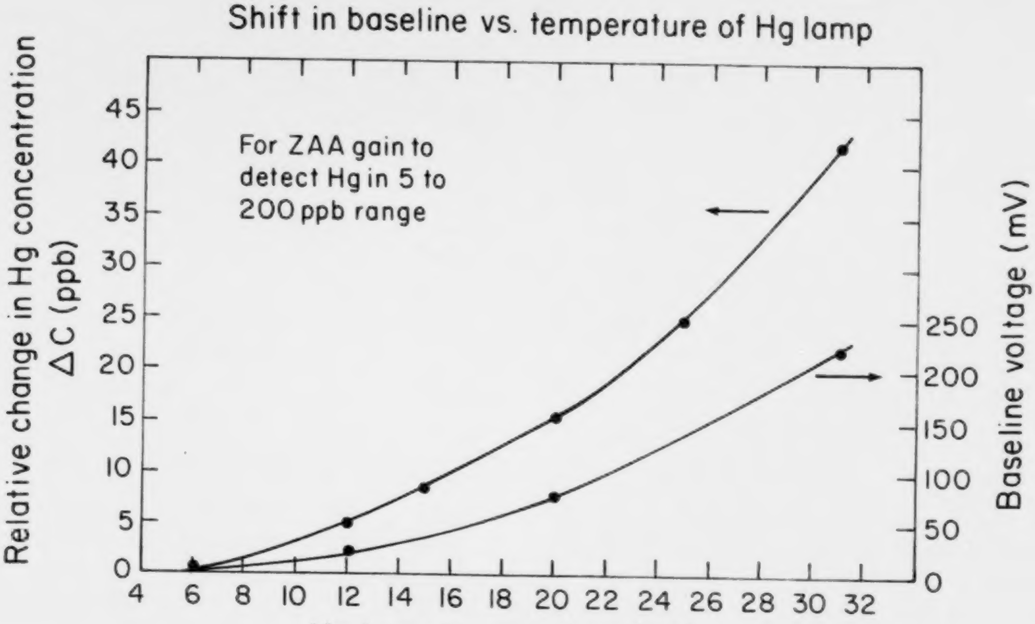

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Figure 8. Change in ZAA output voltage due to temperature-induced self reversal in the absence of mercury in the sample gas. The lower curve shows this effect in terms of baseline voltage. The upper curve shows this effect in terms of apparent mercury concentration. Both curves are normalized to 6° C.

billion (ppb) of mercury. If the lamp is operated at 25°C a variation of ±1°C produces a 6 ppb error. This will be significant for measurements below 60 ppb. However, with the new PPL this problem has been eliminated by simply enclosing the lamp in the water jacket assembly, described above, and coupling it to a small constant-temperature bath mounted within the instrument. The temperature of the PLL can be controlled to within ±0.2°C or ±0.5 ppb mercury. This is approximately equal to the mercury detection limit. This type of temperature control of the light source was not possible with the old EDL.

Another problem with the EDLs was the rf pickup in adjacent instruments (e.g., thermocouples and flow transducers) due to the rf excitation of the argon plasma. This problem has also been eliminated by the use of the PLL. Overall, the mercury PLL offers a significant improvement in ZAA versatility and performance.

Furnace--Absorption Tube Assembly

A new furnace for continuous online analysis of mercury in gas streams has been constructed and successfully operated at 900°C for extended periods. The furnace (Figure 9) is constructed of 1/2 in. o.d., 0.049 in. wall,

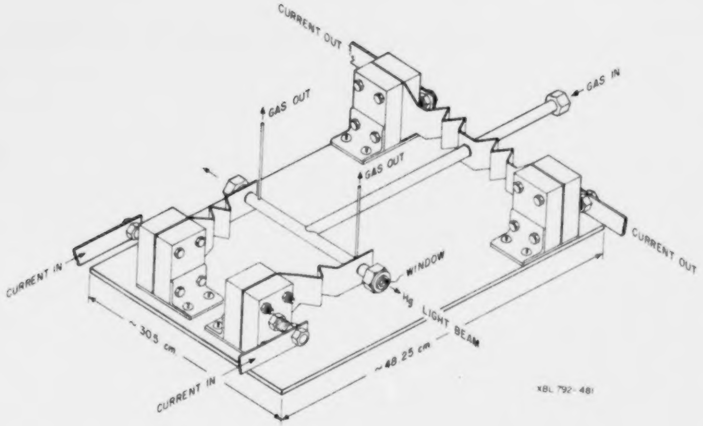

Figure 9. ZAA furnace for on-line analysis of mercury in gas streams.

321 stainless steel (SS) tubing welded into a tee. Incoming gases first pass through an atomization combustion chamber which is maintained at 900°C by joule heating. This chamber is filled with ceramic beads to break up the gas flow and increase the thermal contact area. The gases then pass through a small opening into an absorption chamber which is aligned along the optical path of the spectrometer. The temperature in this chamber is lower since the current in each leg is one-half of the flowing through the atomiztion chamber. Quartz windows at the ends of the absorption chamber pass the 2537 A mercury resonance lines while isolating the hot sample gases from the ambient air. Gases exit the furnace through ports located near each end of the absorption chamber.

Current and the mounting support for the furnace are supplied via variable-cross-section strips of 304 SS welded to the tubing. When the furnace is at operating temperature, the outer ends of these strips are cool, thus preventing the buildup of resistive oxide layers on the power connector surfaces.

The presence of hydrogen sulfide in oil shale offgas and consequent sulfication reactions may create a serious corrosion problem inside the furnace. In an attempt to inhibit corrosion and maximize furnace lifetime, aluminum has been diffused into the surface of the tubing and subsequently oxidized by a process termed alonization. The resulting micro layer of alumina has been shown in laboratory and field experiments to reduce the rate of corrosive attack to stainless steels.

Calibration System

A dynamic calibration system which generates known concentrations of mercury vapor in a carrier gas will be used to calibrate the gas monitor. This sytem, which is shown in Figure 10, is based upon the appartus described by Nelson.[9] Heated air impinges on the surface of a pool of

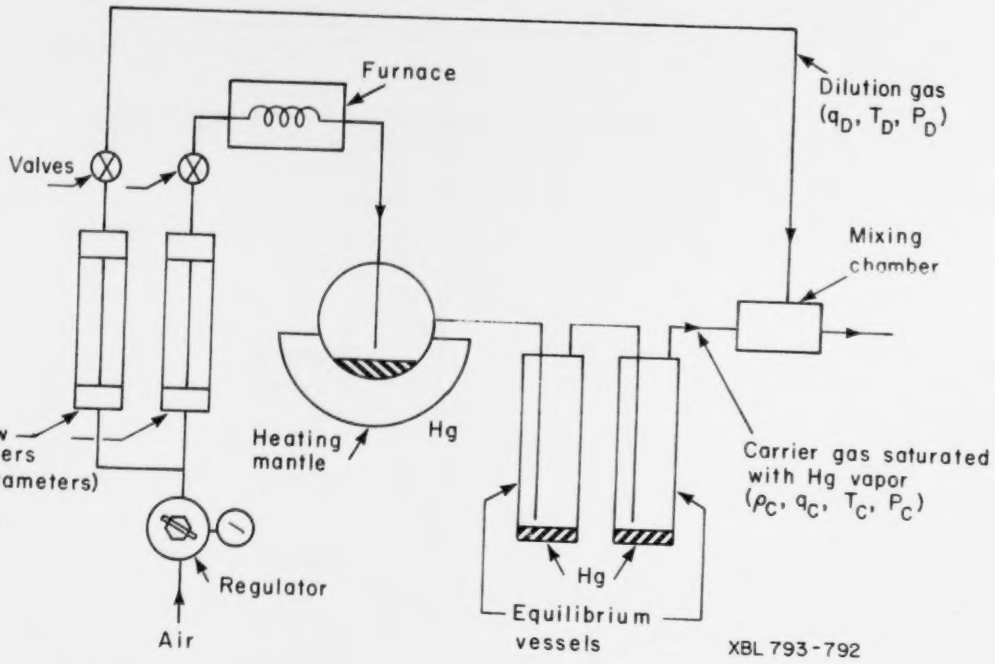

Figure 10. Schematic of mercury calibration system.

mercury warmed to about 60°C. The mercury-laden gas then travels through two successive equilibration vessels; excess mercury condenses, and the gas leaves the vessel saturated with mercury at an accurately determined temperature. The saturated gas is then diluted with mercury-free gas and introduced into the sample line. A range of concentrations is obtained by varying the ratio of mercury calibration gas to dilution gas. With this system it is possible to produce mercury concentrations which range from 0.01 mg/m^3 (1 ppb) to approximately 20 mg/m^3 (2 ppm).

Gas System

The following discussion describes the gas sampling-metering system, develops the necessary calibration formulae, and summarizes the parameters to be measured. The gas handling system is shown in Figure 11. Sample gas, e.g., retort offgas of a given temperature, pressure, and mercury density (T, P, ρ), enters the heated sample line at a volumetric flow rate, q. The heated sample line is to be maintained at approximately 200°C. At point A (Figure 11), oxygen (T_{O_2}, P_{O_2}, q_{O_2}) will be continuously introduced and mixed with the sample gas. This oxygen is used to promote combustion of organics and thus reduce the level of smoke in the ZAA furnace. During calibration, retort offgas will be diverted, and mercury vapor in a carrier gas (T_C, P_C, q_C, ρ_C) will be introduced into the sample line at point A along with dilution gas (T_D, P_D, q_D) and oxygen.

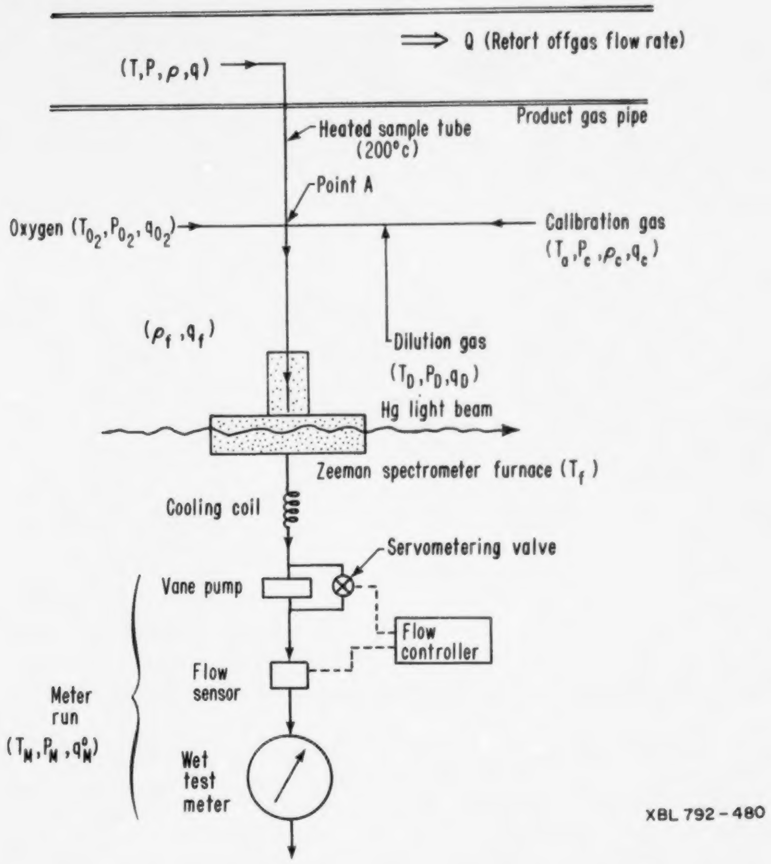

Figure 11. Schematic of gas handling system for ZAA mercury monitor.

TABLE 1. REQUIRED MEASUREMENTS FOR GAS HANDLING SYSTEM

	Temperature	Pressure	Flow
Offgas	T	P	
Oxygen	T_{O_2}	P_{O_2}	q_{O_2}
Calibration gas	T_C	P_C	q_C
Dilution gas	T_D	P_D	q_D
Meter run	T_M	P_M	q_M^o
Ambient conditions	T_{room}	P_{atm}	

The sample and calibration gases then pass into the furnace where they are heated to a constant temperature (900°C) to atomize the mercury. The density of mercury atoms in the furnace is then measured and converted into a voltage response as described above.

It is essential that the furnace be maintained at a constant temperature between calibration runs since the voltage response of the ZAA to a given concentration of mercury varies inversely with temperature. In order to achieve the constant-temperature condition, volumetric flow rate through the furnace (q_M^o) must be held constant. This is to be accomplished by the use of a flow controller. The controller system consists of a flow sensor, which measures the flow downstream of a rotary vane pump, and a servo metering valve in parallel with pump which maintains the desired flow. Flow readings q_M^o are for standard conditions. The flow controller will be calibrated with a wet-test meter located downstream of the controller. Periodic calibration of the flow controller is necessary since the measurement of gas flow by the sensing device depends upon the specific heat of the sample gas. This will change during the course of a retort run. Table 1 summarizes the gas parameters which must be monitored during the analysis of mercury.

To calibrate the ZAA, the voltage response of the instrument must be related to a known density of Hg atoms (ρ_F) entering the furnace. To calculate ρ_F it cannot be assumed that the sample and calibration gases will be at the same temperature initially. Therefore, the Hg densities in both sample and claibration gases must be corrected for temperature differences. In addition, dilution of sample gas by oxygen and calibration gas must be determined. To calculate ρ_F, we assume that the ideal gas law adequately describes changes of state in sample and calibration gas. Density and volumetric flow will be converted to standard conditions (760 mm Hg, 0°C) using Eqs. (1) and (2):

$$\rho^o = \rho \bullet \frac{T}{273} \bullet \frac{760}{P} , \qquad (1)$$

$$q^o = q \bullet \frac{273}{T} \bullet \frac{P}{760} . \qquad (2)$$

T is temperature in °K; P is pressure in mm Hg; ρ is the density of mercury in mg Hg/m^3; q is the volumetric flow rate in m^3/min; and the superscript zero designates standard conditions.

The desnisty ρ_F entering the furnace is the sum of the flow-weighted mercury densities in the sample and the calibration-oxygen lines,

$$\rho_F^o = \rho^o \bullet \frac{q^o}{q_F^o} + \rho_C^o \frac{q_c^o}{q_F^o} , \qquad (3)$$

where

$$q_F^o = q^o + a_C^o + q_D^o + q_{O_2}^o .$$

The measured quantities q_C, q_D and q_{O_2} are converted to standard conditions using Eq. (1) and the measured temperatures and pressures. The standard flow rate of sample gas, q^o, is not determined directly but is obtained by difference between q_M^o and $q_C^o + q_D^o + q_{O_2}^o$.

With the calibration system turned on and the sample gas diverted, the density of mercury entering the furnace becomes, from Eq. (3),

$$\rho_F^o = \rho_C^o \frac{q_C^o}{q_C^o + q_D^o + q^o_{O_2}} \tag{4}$$

The mercury density in the calibration gas at standard conditions ρ_C^o is calculated using Eq. (1):

$$\rho_C^o = \rho_C \frac{T_C}{273} \frac{760}{P_C} ,$$

where $$\rho_C = (3.22\text{x}10^6) \frac{P(Hg)}{T_C} \qquad \frac{\text{mg Hg}}{\text{m}^3}$$

The measured temperature of the calibration gas is T_C, and P(Hg) is the vapor pressure of mercury at T_C obtained from standard tables.

As noted above, a calibration curve can be obtained by varying the mercury calibration gas and dilution gas ratio and recording the ZAA voltage response. When the calibration system is turned off and the sample gas is reintroduced, the calibration curve is used to determine the unknown mercury density ρ^o in the sample gas.

However, during analysis of the sample gas, the mercury density entering the furnace (ρ_F^o) must be corrected for dilution by O_2 introduced at point A. From Eq. (3), we have:

$$\rho_F^o = \rho^o \frac{q^o}{q^o + q^o_{O_2}} \tag{5}$$

An alternate calibration procedure is to inject the calibration gas directly into the sample gas. The concentration ρ_F^o in this case is given by Eq. (3). If matrix effects are a problem, this method will be used to determine the unknown concentration in the sample gas by standard additions.

SUMMARY

This paper describes a technique to continuously measure total mercury in a gas stream in the presence of high concentrations of organics, smoke, oil mist and other interfering substances. The technique employees Zeeman atomic absorption spectroscopy as the mercury detector, which has been successfully used to measure mercury in oil shale offgases. The instrument consist of a light source which provides the 2537 A mercury emission line; a furnace-absorption tube assembly where the sample is vaporized and swept into the light path and a detector which converts the signal into an ac voltage for processing. Sample gas is heated to 900°C in the furnace-absorption tube assembly aligned with the optical axis of the ZAA spectrometer. The 2537 A mercury emission line (π) and a reference line (σ) are generated by a single discharge lamp operated in a 15 kG magnetic field. The difference between the π and σ components is taken by a lock-in-amplifier and converted to a signal which is proportional to the amount of mercury in the gas.

ACKNOWLEDGEMENTS

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A SAMPLING AND ANALYSIS PROCEDURE FOR GASEOUS SULFUR COMPOUNDS FROM FOSSIL FUEL CONVERSION

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ABSTRACT

For some three decades, several alternative processes to convert fossil fuels to liquid and gaseous fuels have been under development. These processes generate, among other effluents, a gas stream containing hydrogen, carbon dioxide, carbon monoxide, hydrocarbons, and sulfur compounds. A sampling and analysis methodology is described for reactive gaseous sulfur compounds including hydrogen sulfide, carbonyl sulfide, sulfur dioxide, methyl mercaptan, ethyl mercaptan, carbon disulfide, and thiophene contained in gas streams as those from developmental processes. An all-glass system is used to collect and store the gas samples. An all-Teflon gas chromatographic analysis system utilizing a thermal conductivity and a dual-flame photometric detector is used for the analysis. Quality control procedures for accurate quantification are described. Typical chromatograms are shown, and conditions for analysis are listed.

INTRODUCTION

In recent years, considerable research has been devoted to developing efficient ways to convert fossil fuels--coal and oil shale--to more suitable forms of energy. In 1926, about 150 manufacturers were producing gas from coal worldwide, with about 12,000 units operating in the United States. The availability of clean natural gas and pipeline systems led to the demise of these gasifiers. With the projected energy shortage, interest in coal gasification has revived. Some 68 different gasification processes have been identified. Six leading units include the Lurgi, Wellman-Galusha, Woodall-Duckhamn, Koppers-Totzek, Winkler, and Chapman-Wilputte. Second generation processes for the production of synthetic fuel gas from coal include the Hygas, Bigas, and Synthane Processes.

With regard to oil shale, some eight projects are at various stages of development for the commercial production of synthetic crude oil in Colorado and Utah. Additionally, at least 14 major research, pilot plant, or demonstration projects are currently underway throughout the United States.[1] [2]

The preliminary outlook is bright for the developmental coal and oil shale conversion processes because respectable recovery of the heating value can be made without undue technical problems. However, various environmental constraints remain to be fully investigated.[3] Of concern to this study is the environmental impact posed by sulfur-containing compounds in the product gas.

It is instructive to compare typical coals and oil shales. Table 1 shows the sulfur levels in the raw fuels and H_2S and COS levels in the gas streams obtained from the processes mentioned. The data indicate that a procedure capable of measuring sulfur compounds over a wide range is needed for use in fossil fuel conversion processes. Additionally, a dearth of information, especially for shale gas, exists in the literature concerning the content of sulfur compounds other than H_2S and COS. Of particular concern are mercaptans, carbon disulfide, and thiophene.

Drabkin[4] used an elaborate scrubbing and colorimetric scheme to determine these compounds in gas from a Russian shale containing 2 percent sulfur. In recent years, however, gas chromatography-flame photometric detection (GC-FPD) has become a very popular method for individual sulfur compound determinations[6] [7] [8] [9] because of its speed, specificity, and sensitivity. However, many difficulties can arise when the gases are present in widely differing concentration levels. H_2S is the predominant sulfur gas from high-sulfur fuels, but it is present in such concentrations that the

TABLE 1. SULFUR IN RAW FUELS AND PRODUCT GASES

	Colorado Green River+ (eocene) Shale	Michigan+ Antrim (Devonian) Shale	Illinois No. 6 Coal	Wyoming Subbituminous Coal
Sulfur, wt %	0.5	3.5	3.0	0.6
H_2S, ppm	<100+	4,000	12,000	900
COS, ppm	<100=	1,000	40	30
Process	Ex situ 10 ton batch retort	Ex situ 10 ton batch retort	Low Btu semi-batch gasification*	Low Btu semi-batch gasification*
Site	LETC	LETC	RTI Run 23	RTI Run 35

LETC--Laramie Energy Technology Center.
RTI--Research Triangel Institute.
*H_2S and COS levels are integrated averages over the duration of the batch process.
+As reported in Reference 5.
=Not indicated by mass spectrometer.

FPD will saturate even with small samples. Microsamples can be used, but then the detectivity of other gases will be lost. Other problems associated with the FPD are its nonlinearity, compound dependency, and reduced response because of an interfering hydrocarbon matrix eluting with the sulfur species.[10 11 12] Problems are associated with the GC system as well, including strong absorption of the trace sulfur gases on the column packing and reaction on the walls of the columns and the sampling devices.

The purpose of this paper is to present a reliable and efficient method that can be readily applied to measurement of H_2S, COS, CH_3SH, C_2H_6S, CS_2, and thiophene in the off gas from fossil fuel conversion processes. A dual-column, dual-detector GC system has solved many problems mentioned above.

EXPERIMENTAL

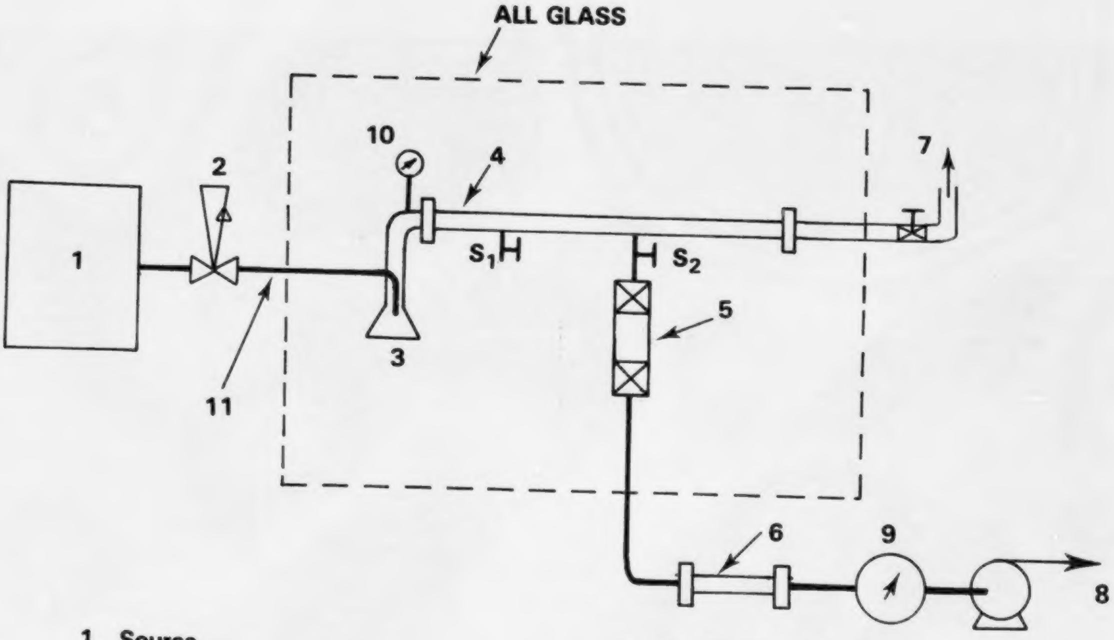
Sampling System

Sulfur gases can be sampled from the process under study using the all-glass Teflon system shown in Figure 1. A pressure letdown device is required only when the gases are to be sampled from a high-pressure zone. An all-glass Teflon system is necessary to prevent degradation of the reactive sulfur compounds. The storage containers (Figure 2) have two high-vacuum stopcocks so that sample dilution can be prevented if repeat or additional analyses are required. Samples are stored in a temperature-controlled box (50°C) until ready for analysis (Figure 3). The box provides safe storage and transport. An estimated moisture content in the samples for which this procedure was effective was 0.8 percent or less.

GC Sample Injection and Analysis System

A Varian 3700 gas chromatograph (GC) equipped with a thermal conductivity detector (TC) and a dual-flame FPD was used in this study. Modifications were made to the pneumatics to allow for gas sample injection at subatmospheric and superatmospheric pressure. A 6 ft. by 1/8 in. Teflon (FEP) column packed with Carbopack B/1.5% XE-60/1% H_3PO_4 obtained from Supelco, Inc., was used with the FPD. Grade 0.5 helium and grade 0.1 hydrogen obtained from Airco were used as carrier and fuel gases. A Bendix clean air system was used to provide dry hydrocarbon-free air to the FPD. Gas flows were controlled with both pressure regulators and flow control needle valves. A 6 ft. by 1/8 in. Porapak-N column was used with the TC detector for H_2S and COS analyses at high levels (>400 ppm). Standard mixtures containing certified amount of H_2S, COS CS_2, CH_3SH, C_2H_6S, and thiophene, individually, in N_2 were obtained from Scott Environmental Technology, Inc., for detector calibrations. Conditions of analysis are summarized in Table 2.

A simplified schematic of the GC injection system is shown in Figure 4. The sample injection valve was made of inert high-nickel hastalloy-C. The Heise gauge has a range from -760 to 1500 mm Hg gauge in 2 mm graduations. The vacuum pump was capable of evacuating the system to 10^{-4} torr. An



1. Source
2. Pressure Letdown Device
3. Glass, Entrained Moisture, Trap
4. 1 in Glass Manifold
5. Glass Sample Storage Container with Two High-Vacuum Stopcocks (Figure 3)
6. Drierite Moisture Traps
7. Valve
8. Pump
9. Dry Gas Meter
10. Pressure Gauge (0-15 psig)
11. Corrugated Teflon Tubing

Figure 1. Schematic of sampling system.

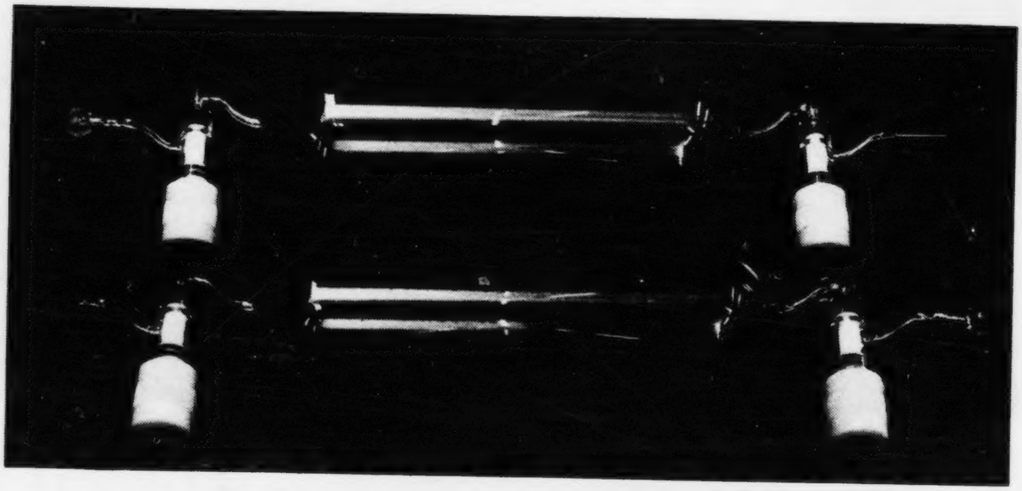


Figure 2. Glass containers with 0-4 mm ultratorr stopcocks.

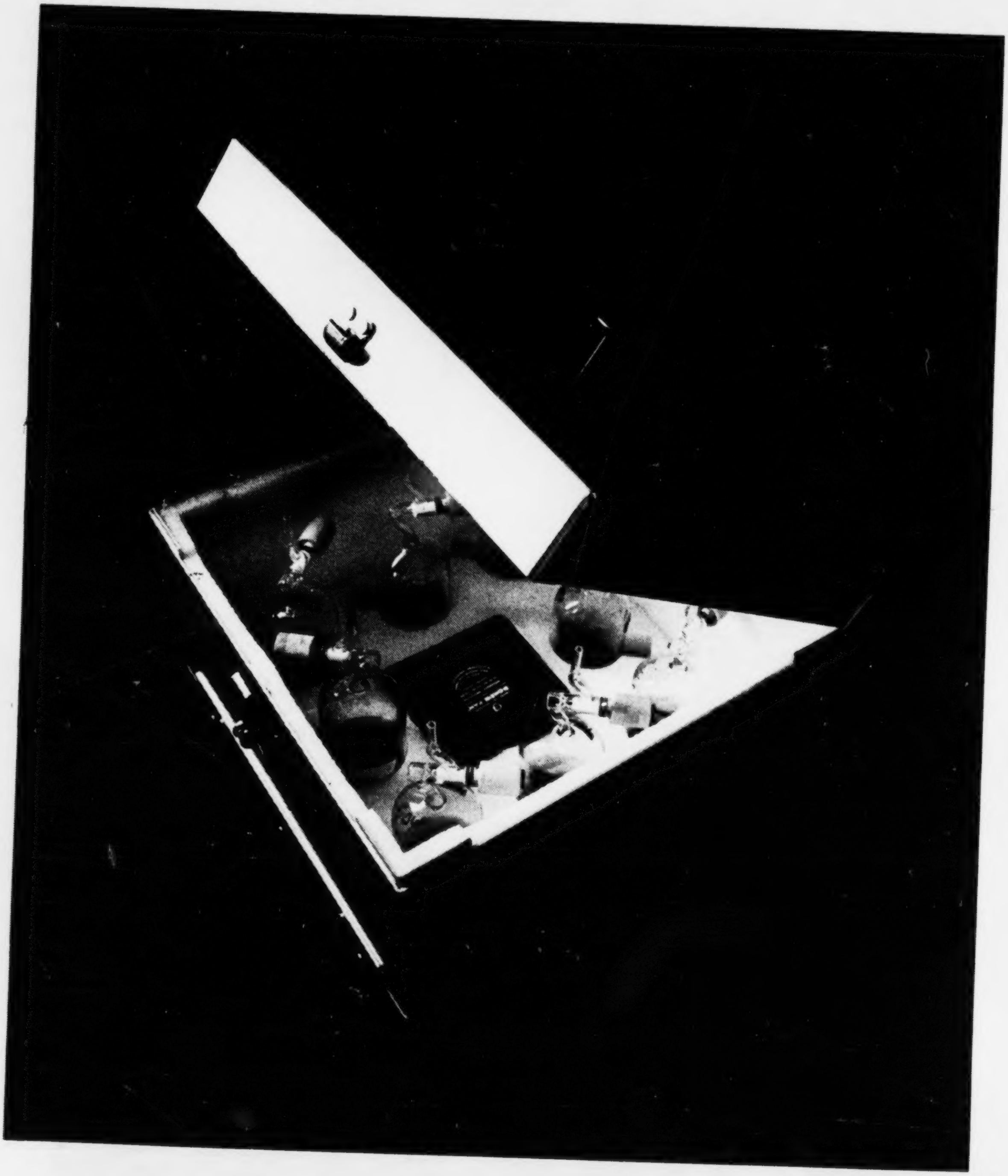


Figure 3. Constant temperature sample storage box.

TABLE 2. CONDITIONS FOR ANALYSIS

	FPD	TC
Column	Carbopack B/1.5% x E60/1% H_3PO_4 6 ft x 1/8 in Teflon	Porapak N, 6 ft x 1/8 in Teflon
Helium carrier	30 ml/min	30 ml/min
Detector temperature	150°C	200°C
Column temperature	50°C for 2 min 30°C/min to 130°C Hold 5 min	70°C Isothermal

additional sample injection valve (not shown) was used for the second column and detector. For the TC detector, a column backflush valve (not shown) was used to prevent previous sample analyses from interfering with the sample being analyzed. All gas lines were Teflon; a 1-ml Teflon sample loop was used, and all fittings from the sample bottle to beyond the sample loop were glass or Teflon. All valves were installed in heated ovens, and sample transfer lines were kept to minimum practicable length. Dead volumes were kept to a minimum.

Procedure

A diagram of the FPD explaining the two air supplies is given by Patterson et al.[13] Gas flow rates for maximum sensitivity in the dual-flame mode were He: 30 ml/min; H_2: 140 ml/min; air 2: 80 ml/min; and air 1: 166 ml/min. The detector could also be used in the single-flame mode by shutting off air 2. For maximum sensitivity, air 1 then had to be increased to 205 ml/min.

Prior to injection, the sample loop and connection were adequately flushed with the sample. The desired amount of sample, measured in terms of absolute pressure, was then trapped in the loop and injected with the valve. An absolute pressure range of 50 mm Hg to 1,200 mm Hg was used. It was possible to generate calibration curves from a single standard using different pressures. Peak areas were measured using an HP 3352 laboratory computer.

For the thermal conductivity detector, a linear calibration was observed over the range of H_2S and COS concentrations studied. For the FPD, a log-log calibration was necessary, both in the single- and dual-flame modes. Typically, the following relationship was observed.

$$A = C\ (S)^n \tag{1}$$

A = peak area
C = constant
S = sulfur mass or concentration
n = exponent (1.67 to 2 depending on compound) COS; 1.82, CS_2; 1.83, thiophene; 1.67, CH_3SH; 2.00, C_2H_6S; 1.9 in the dual-flame mode for conditions listed in Table 2.

Industrial samples obtained from various fuel conversion facilities were analyzed using the above procedures. Subatomspheric injection was termendously advantageous because of the ease with which the sample size could be varied when required, and calibrations could be performed for each compound.

RESULTS AND DISCUSSION

Figure 5 demonstrates the repeatability of the analysis system. A relative standard deviation of less than 3 percent was obtained on a sample size of about 1 ng sulfur (1.12 ppm SO_2 in 1 ml loop at ambient conditions). Figure 6 shows a typical FPD calibration plot on log-log paper.

Similar calibrations were performed for other sulfur species. The single-flame mode on the FPD was found to be about 1.5 times more sensitive than the dual-flame mode. The ordinate of area/$\sqrt{}$height instead of area is shown to collapse several sulfur species into one curve. The abscissa could also be plotted as (ppm x mm Hg) instead of ng S, since both are proportional according to the ideal gas law.

Figures 7 and 8 show the desired separations of actual samples obtained from the RTI coal gasifier. Similar compounds are expected to be present in shale gas. This is demonstrated in Table 3 where sulfur compounds in gases from three processes have been sampled and measured using the procedure described. The Michigan shale has a high sulfur content resulting in high amounts of sulfur emissions. The analysis is not representative of low-sulfur shales like those from Green River, etc. Qualitatively, however, similar compounds are expected.

QUALITY CONTROL

The sulfur compounds must be stable in the glass containers until analyzed. This was tested for samples obtained from coal gasification (Table 4). As seen, the concentration change is generally less than 5 percent over a period of more than 100 hour. Stability of some individual sulfur species in the glass containers in the presence of ambient air was also tested (Figure 9) down to less than 1 ppm. A stepwise dilution of partially evacuated glass bulbs with ambient air was carried out and followed by a series of measurements over a period of several hours to determine

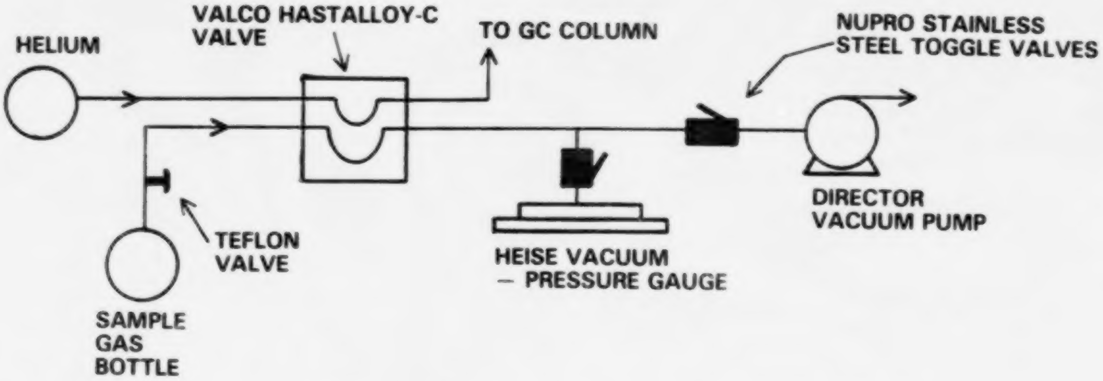


Figure 4. Schematic of GS injection system.

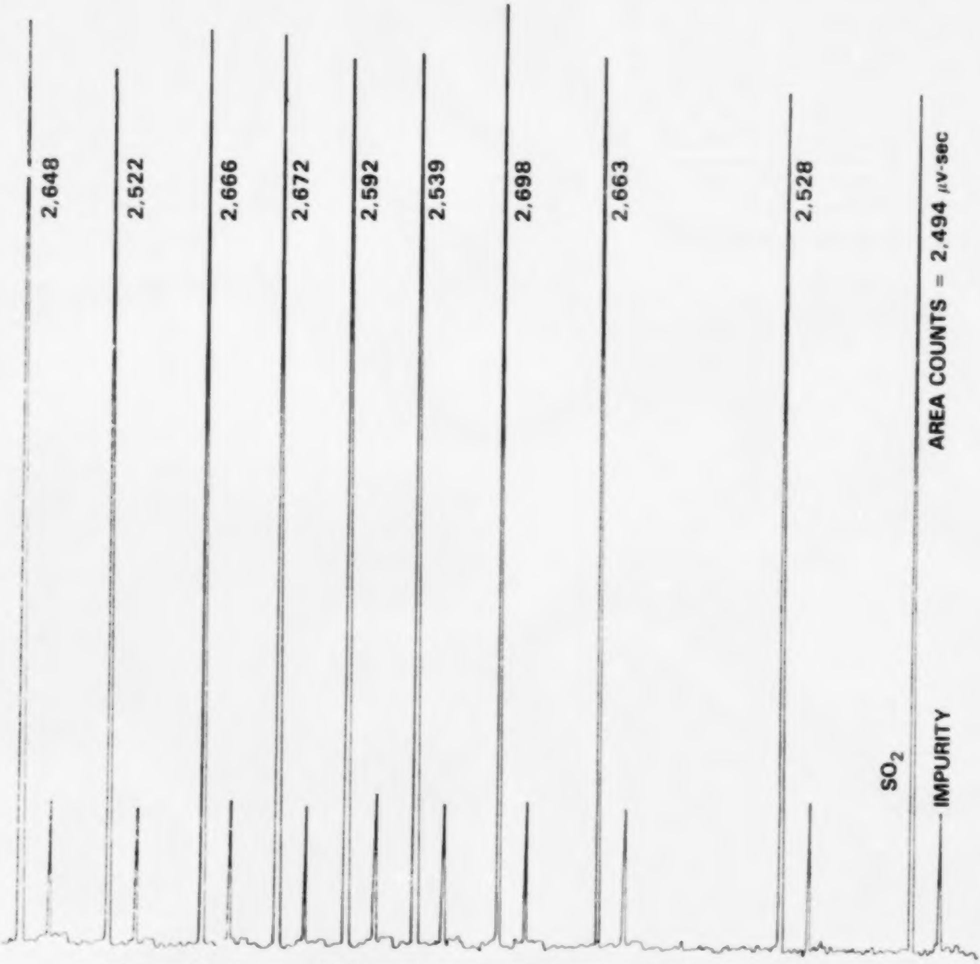


Figure 5. Repeatability of system for 1 mL-sample of 1.12 ppm SO_2 in the dual-flame mode.

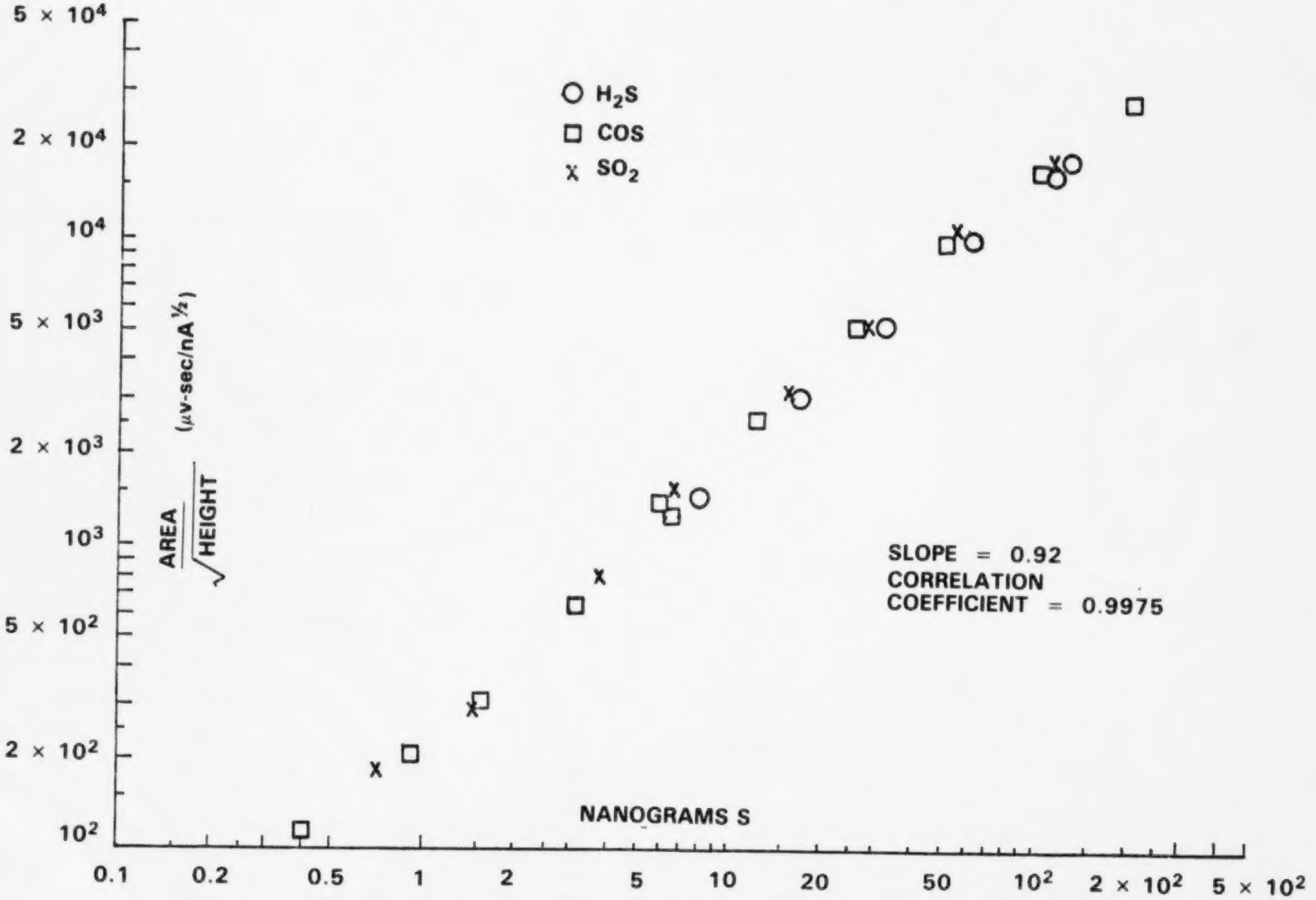


Figure 6. Nanograms sulfur vs. area/$\sqrt{\text{height}}$ for H_2S, COS, and SO_2 in the dual-flame mode.

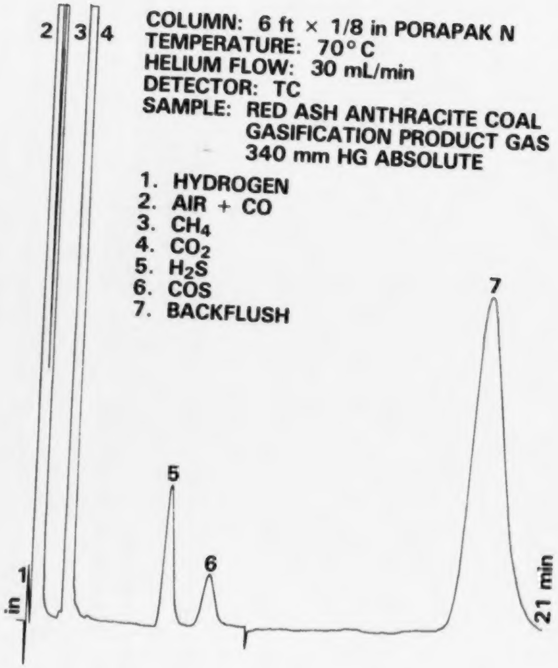


Figure 7. Analysis of H_2S and COS.

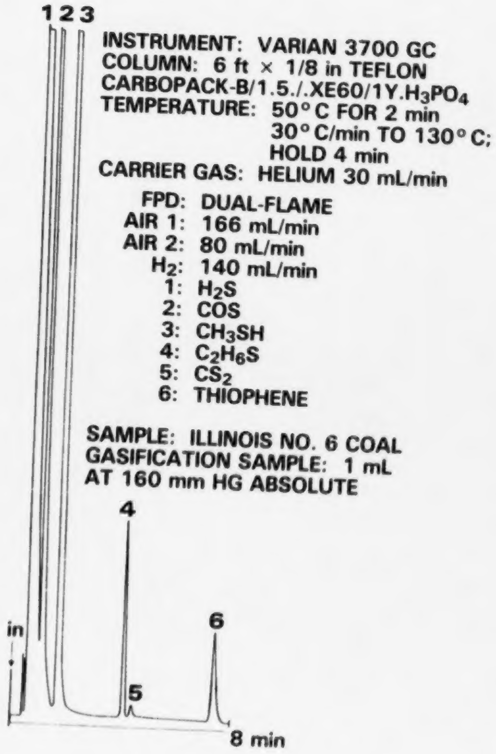


Figure 8. Separation of gaseous sulfur compounds.

TABLE 3. ANALYSES OF SULFUR COMPOUNDS IN OFFGASES FROM FUEL CONVERSION FACILITIES

Fuel	Illinois No. 6 Coal	Devolatilized W. Kentucky/#1 Coal	Michigan Antrim Shale
Sulfur wt %	3.0	2.9	3.5
H_2S (ppm)	12,000	5,000	7,100
COS (ppm)	50	280	600
CH_3SH (ppm)	20	<1	40
C_2H_6S (ppm)	10	<1	30
CS_2 (ppm)	4	2	270
Thiophene (ppm)	120	~0.4	17
Site	RTI test #6	NCSU	LETC
Process	Semibatch gasification	Continuous fluid bed gasification	Oil shale batch retorting

NCSU--North Carolina State University coal gasification facility.

stability. The solid and dashed lines represent calculated values from dilution factors whereas the discrete points represent measured values. Agreement is generally good except for H_2S at sub-ppm levels. The objective of these measurements were to test the validity of the described sampling and analysis procedure for both sources (concentrate), as well as fugitive emissions (dilute) from fossil fuel conversion facilities.

Log-log plots must be used for calibration of the FPD. Use of the square root signal linearizer built into commercial FPD electrometers is not recommended since, as given earlier, the exponent of equation (1) is not always 2. As demonstrated by Farwell and coworkers,[14] the use of the square root mode could easily result in as much as 70 percent error. Individual calibration is recommended for each sulfur compound, although reasonable determinations can be made by using calibration plot of $A\sqrt{H}$ vs. ng S or ppm by volume as shown in Figure 5, since it collapses several sulfur species into one plot.

A final problem with FPD, as mentioned in the introduction, is the quenching effect of hydrocarbons on sulfur response. The dual-flame FPD minimizes this problem, as claimed by Patterson et al.,[15] by separating the regions of sample decomposition and light emissions. This was tested on a coal gasifier product gas sample containing a large background of hydrocarbons (sample was obtained during the pyrolysis period), which was analyzed in the two modes. Figure 10 shows the analysis. At the same attenuation, no CS_2 response is seen in the single-flame mode even though a larger thiophene response is obtained. FID response under identical conditions shows a large hydrocarbon background as CS_2 elutes.

TABLE 4. SAMPLE STABILITY CHECK

Sample No.*	Time (hr)	COS (ppm vol)	CH_3SH (ppm vol)	C_2H_6S (ppm vol)	CS_2 (ppm vol)	Thiophene (ppm vol)
S1 (7 min from coal drop)	3	550	39	20	230	250
	28	540	37	19	220	250
	49	530	37	19	220	250
	74	530	36	19	220	240
	98	540	38	20	220	250
	123	530	36	19	220	240
	147	510	35	18	210	230
S2 (16 min)	3	440	17	9	140	150
	28	420	16	9	140	150
	49	420	15	8	130	150
	74	420	16	9	140	150
	98	430	16	7	140	150
	123	410	15	7	130	140
	147	410	16	6	130	140
S3 (86 min)	3	150	<1	<1	<1	<1
	28	140				
	49	140				
	74	130				
	74	130				
	98	140				
	123	130				
	147	130				

*Samples obtained from low-Btu semibatch gasification of W. Kentucky #9 coal.

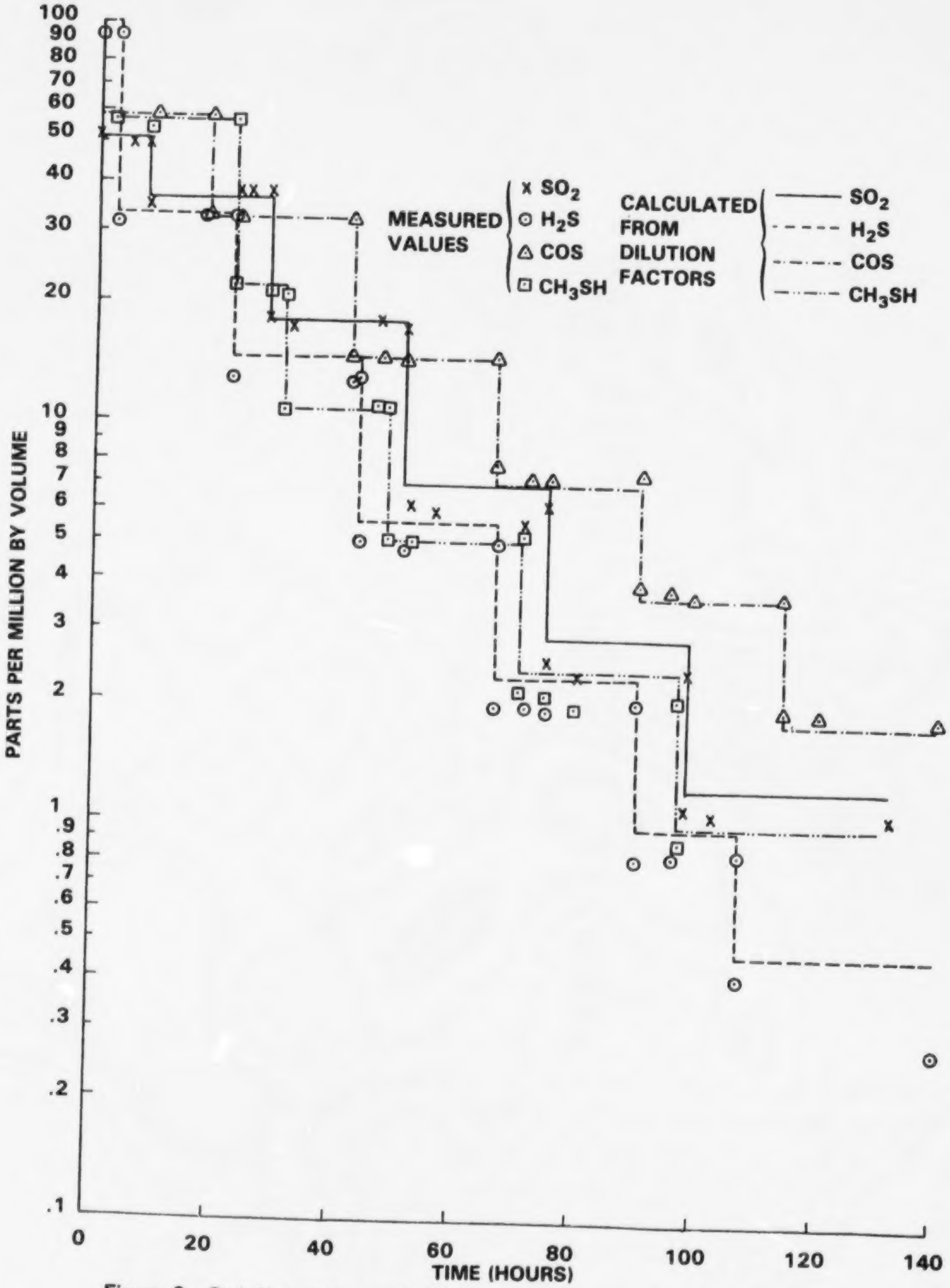
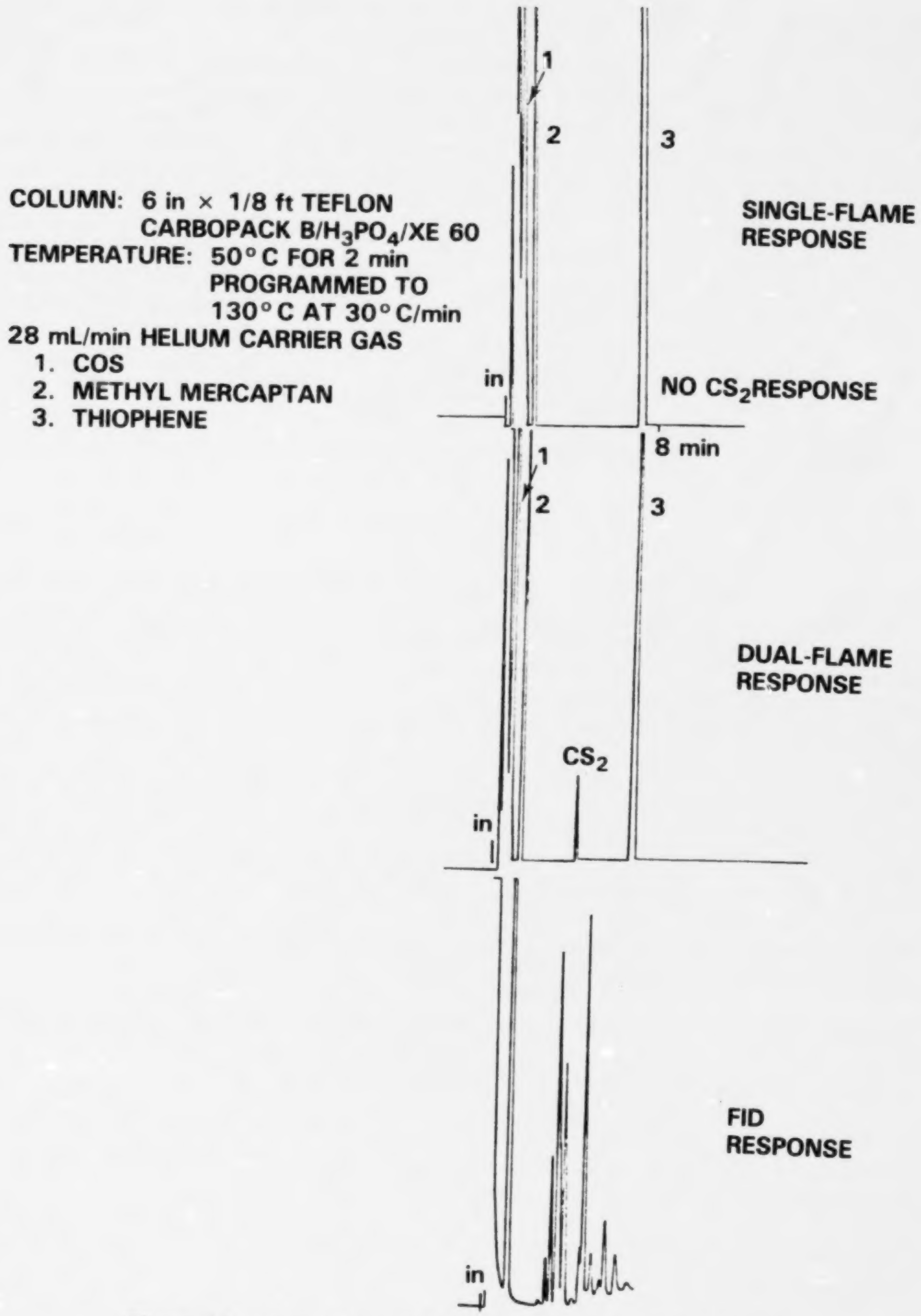


Figure 9. Stability of low molecular weight sulfur species in glass containers in presence of ambient air.



COLUMN: 6 in × 1/8 ft TEFLON
CARBOPACK B/H_3PO_4/XE 60
TEMPERATURE: 50° C FOR 2 min
PROGRAMMED TO
130° C AT 30° C/min
28 mL/min HELIUM CARRIER GAS

1. COS
2. METHYL MERCAPTAN
3. THIOPHENE

Figure 10. Comparison of dual- and single-flame modes for a coal gasifier product gas.

Another way to check the hydrocarbon effect is to analyze the same sample repeatedly and see if identical responses are obtained. The hydrocarbons eluting from previous injections could quench the response for the sample being analyzed. For the dual-flame mode, repeated analysis of the same sample gave identical response. On the other hand, it was not possible to reproduce the response when the same sample was repeatedly analyzed in the single-flame mode. This was attributed to quenching because of hydrocarbons eluting from previous analyses. As much as 75 percent relatively different responses have been observed for CH_3SH, C_2H_6S, and CS_2 present in samples analyzed repetitively. A backflush following each sample would reduce the errors involved, but this, of course, adds to the time and cost of analysis. Even when the backflush is added, the response will still be nonuniform, depending on the amount of hydrocarbons present in the sample. Thus, the dual-flame detector is a suitable choice for samples from fossil fuel conversion even though its minimum detection limit is not as good as the single-flame detector. However, for fugitive or ambient samples where lower detection limits are required, the single-flame detector could be more suitable.

ACKNOWLEDGMENTS

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FUGITIVE DUST AND OFFGAS ANALYSIS METHODS APPLIED AT THE PARAHO FACILITY

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INTRODUCTION

BACKGROUND

An environmental assessment of oil shale processes was recently completed for the USEPA by TRW. As part of the assessment effort, TRW conducted a sampling and analysis program at the Paraho oil shale demonstration plant in Anvil Points, Colorado, in 1976.[1] This work was done in close cooperation with the Paraho operating company, Development Engineering, Inc. (DEI).

A strong recommendation resulting from this prior work was that a comprehensive fugitive dust survey should be conducted at the Anvil Points site, in anticipation of future studies for dust control related to mining, crushing, and material handling operations. In addition, retort offgas analyses were also recommended as a first step in characterizing retort gas as a potential fuel, and its combustion products.

AIMS OF THE TEST PROGRAM

The fugitive dust program objectives included: 1) determining the sources of fugitive dust; 2) noting related meteorological characteristics; 3) quantitatively evaluating the total suspended particulates (TSP) over and above natural background TSP values at various distances from the dust sources; and 4) determining particulate size distribution at the TSP measurement locations.

In addition to the mass measurements, chemical composition of particulate matter was also defined as a program measurement objective. Both inorganic elemental analysis and organic classifications were sought. These constituent analyses helped to further characterize particulate matter, and they also provided useful clues concerning the particulate-generating sources.

The offgas measurement objectives incorporated the quantitative determination of organic constituents (C_1-C_{12}), combustion products, nitrogen-based constitutents, sulfur-based constituents, and volatile trace elements.

THE PARAHO PROCESS

The demonstration plant operations, indicated schematically in Figure 1, consisted of mining, raw shale hauling, crushing and screening, retorting, and retorted shale disposal. Crude shale oil was stored in tanks for subsequent shipment to an offsite refinery. The heart of the demonstration plant is the Paraho retort (Figure 2), which can process about 400 metric tons per day.

Provision has been made for operating the retort in either the direct mode or indirect mode. In the direct mode the carbon on the retorted shale is burned in the combustion zone to provide the principal fuel for the process. Low calorie retort gases are recycled to both the combustion zone and the gas preheating zone. In the indirect mode heat for retorting is supplied by recycling offgases through an external furnace, thus eliminating combustion in the retort and producing a high heating value, 8000 kcal/std cu meter offgas.

In either mode of operation, raw shale is fed into the top of a Paraho retort and passed downward by gravity successively through a mist formation and preheating zone, a retorting zone, either a combustion zone (direct mode) or heating zone (indirect mode), and finally, a residue cooling and gas preheating zone. It is discharged through a hydraulically-operated grate, which controls the throughput rate and maintains even flow across the retort. The retorted shale is discharged from the retort at about 150°C (300°F), and sent to the shale disposal area.

The shale vapors produced in the retorting zone are cooled to a stable mist by the incoming raw shale (which is thereby preheated), and leave the retort. This mist is sent to a condenser, and finally a wet electrostatic precipitator, for oil separation. The resulting shale oil is transported to storage.

The demonstration plant differs considerably from a commercial facility design, so that it cannot be considered a scale model of a full-size operation. The product gas at the demonstration plant was combusted in a thermal oxidizer prior to atmospheric discharge; in a commercial facility this gas would be cleaned and used as a fuel in process heaters and boilers. Material handling in a commercial plant would most likely rely on conveyors, rather than trucks, and the disposal of retorted shale would be a major portion of the operation.

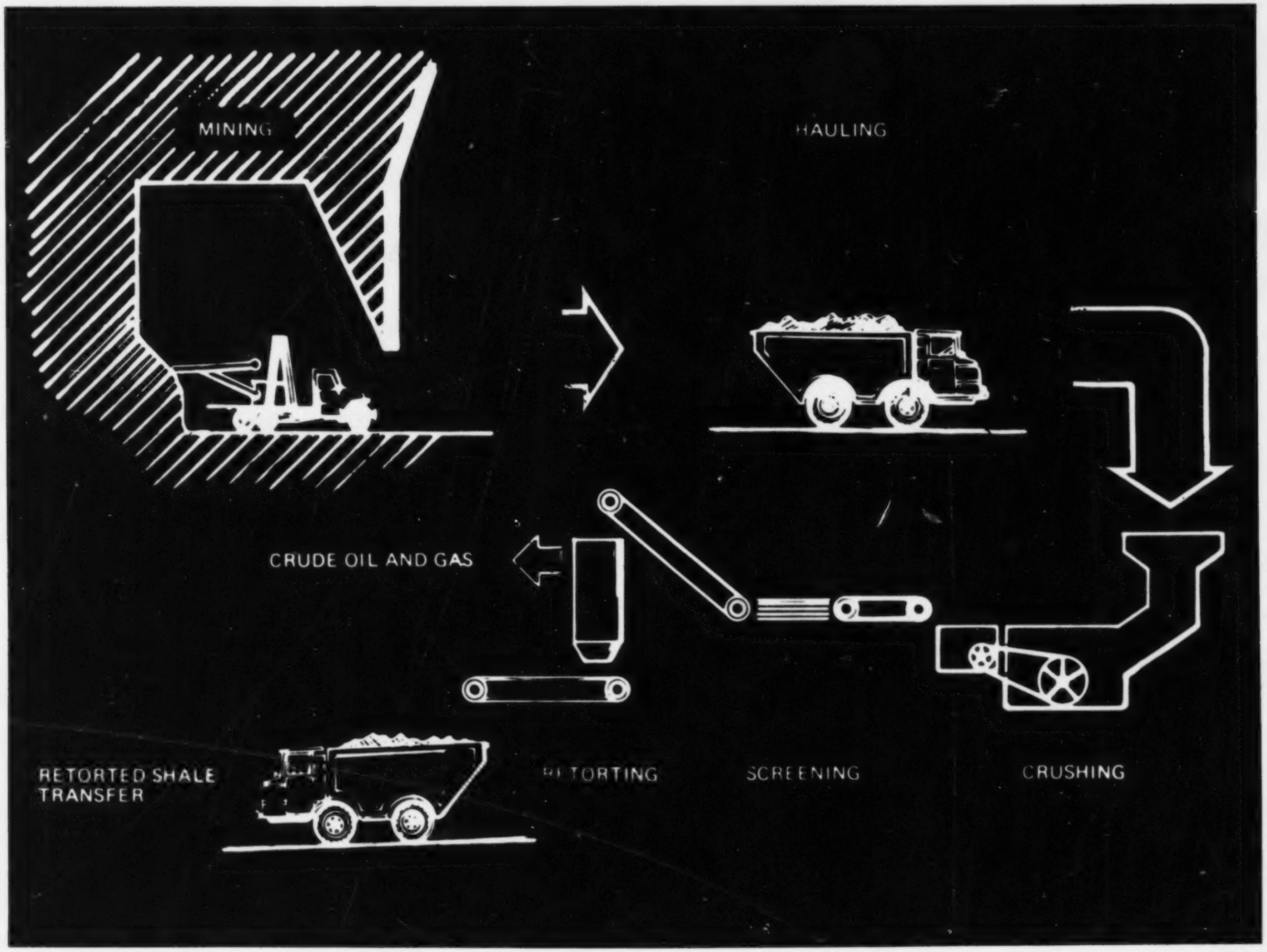
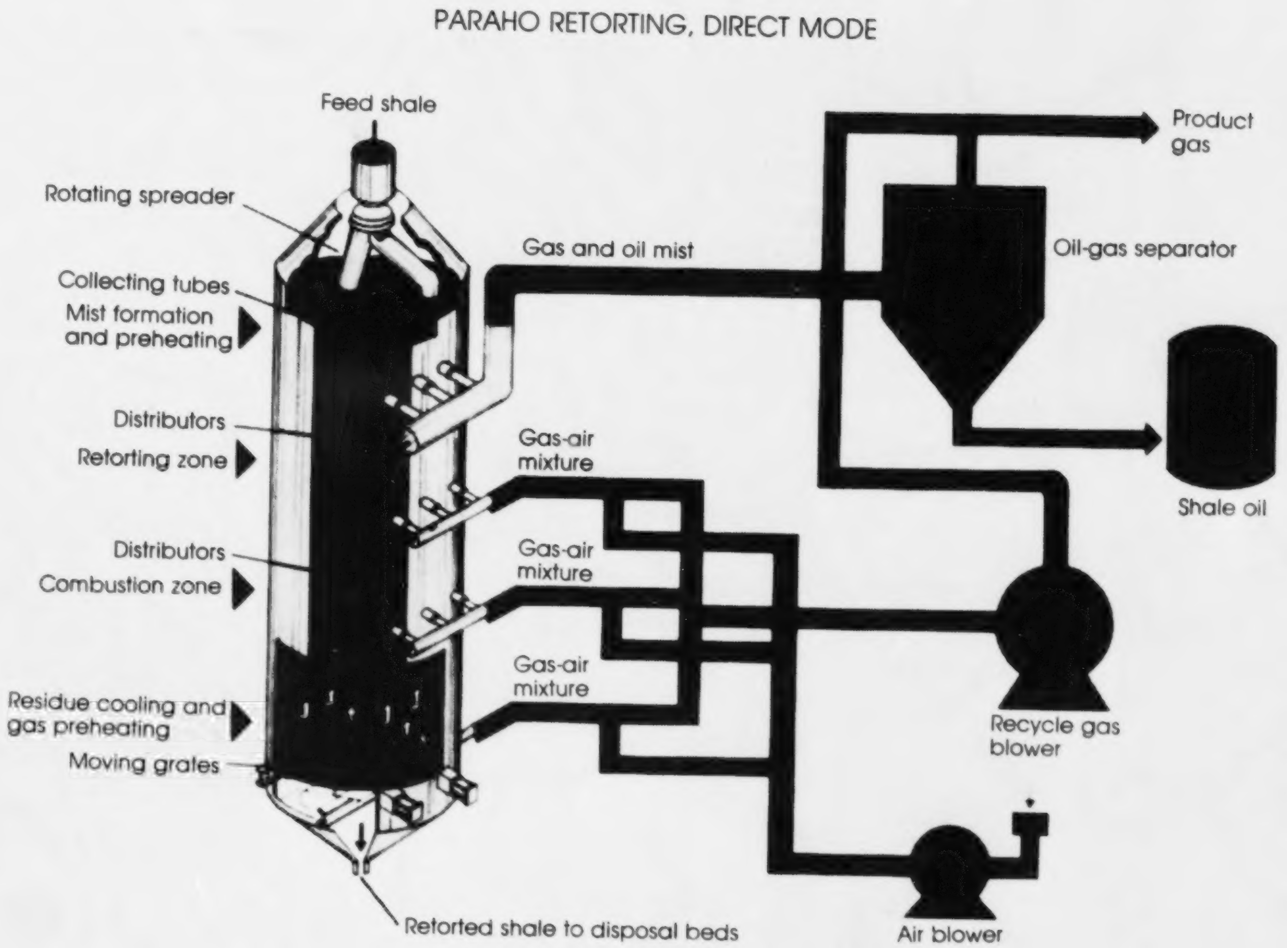


Figure 1. Schematic of Anvil Points Mining and Material Handling Operations.



PARAHO RETORTING, DIRECT MODE

Figure 2. Schematic of Paraho Retort.

SAMPLING AND ANALYSIS PROGRAM

Fugitive Dust Program Execution

The principal dust collection devices were high-volume samplers (General Metal Works Models 2000 and 2310). These were supplemented, as required by the test plan, by cascade impaction samplers (Sierra Instruments, Model 235) determining particle size distribution. The sampling locations and area designations are given in the local contour map (Figure 3) and the test matrix (Table 1) respectively. As indicated in Table 1, dust collection took place in the vicinity of mining, hauling, crushing and discharging operations. The Anvil Points mine ventilation system consists of fresh air forced through one adit, circulation to the back of the mine, and exhaust from two remaining adits. High-volume samplers were used at the mine mouth for the fugitive dusts carried out in the exhaust air through the two adits. Except for the mine, meteorological instrumentation was also provided at each collection location to continuously record wind direction and velocity.

The sampling schedule was arranged for a continuous 4-week effort, in an attempt to include some statistical variation of sample characteristics during the course of the program. As indicted by the test matrix (Table 1), measurements in the vicinity of the crusher were not emphasized. The crushing equipment furnished by the U.S. Navy, was used as an expedient during the limited duration research and development program conducted by DEI.

TABLE 1. TEST MATRIX

Sources	No. sampling locations	Total No. samples for TSP	Total No. size distribution	Total No. inorganic and organic analyses
				(Each category)
Mine adits	2	40	8	4
Haul road	3	90	12	6
Crushing area	3	15	6	3
Spent shale transfer	3	30	12	6

The required complement of high-volume samplers, portable generators, and meteorological instruments were deployed at the Anvil Points site according to the final test plan. High-volume samplers are shown positioned at the retorted shale transfer area (Figure 4) and adjacent to the haul road (Figure 5). The collectors located near each source consisted of a one upwind-two downwind configuration, with the exception of the mine mouth. As in most mountain valley terrains, there was a strong upslope wind during midday, and patterns were variable, so that close surveillance was required

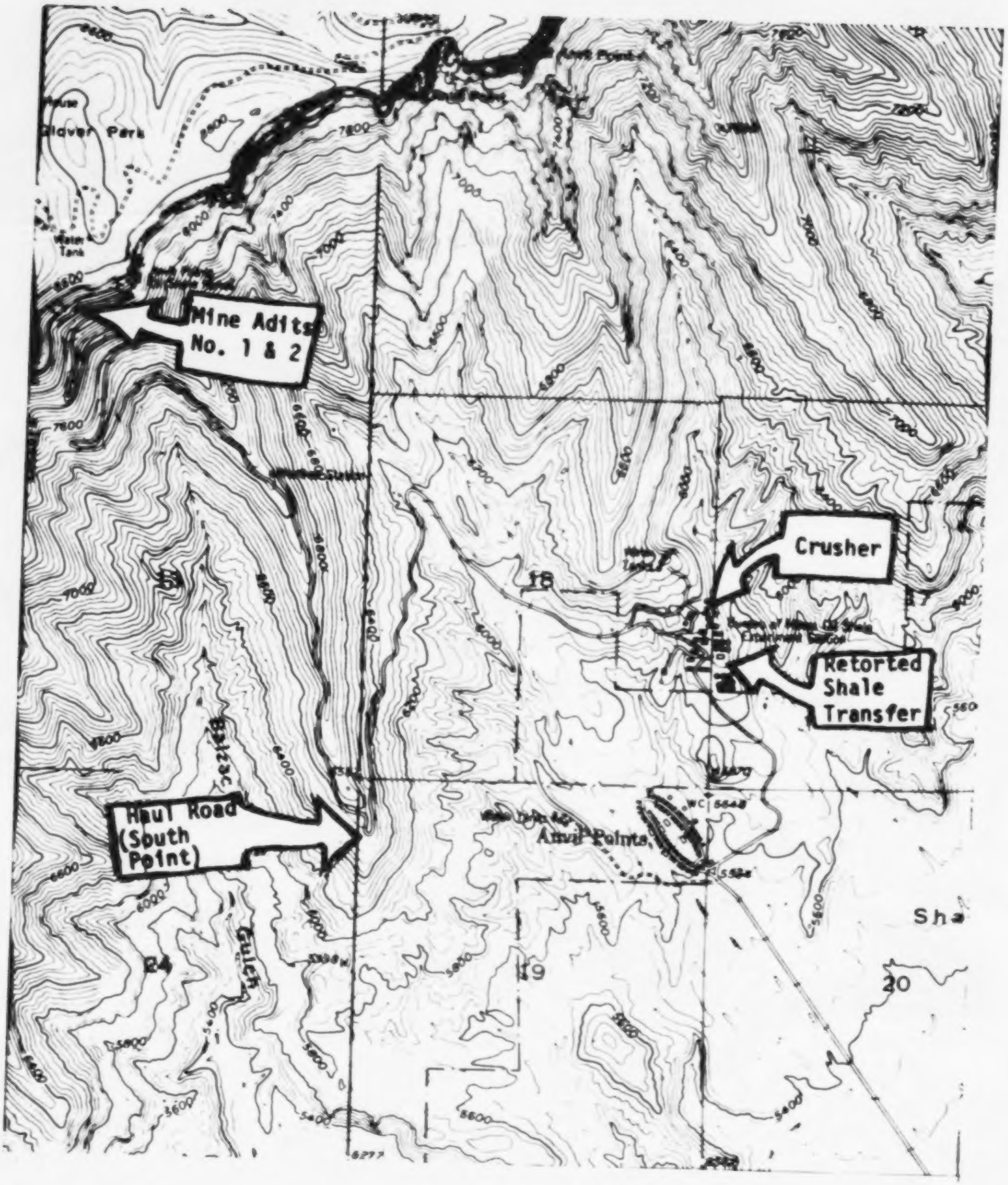


Figure 3. General Locations of Fugitive Dust Sampling.

Figure 4. High-Vol Samples at Retorted Shale Disposal Area.

Figure 5. High-Vol Samplers and Meteorological Station Near Haul Road.

in order to determine when a collector was in an upwind or downwind position, and manual switchovers were done as required.

Data Reduction and Quality Assurance for Dust Sampling

The period of sampling varied, depending on the amount of sample desired and proximity to a source. Although a nominal 1-hour sampling period was usually sufficient, rough filter weighings in the field were used to provide assurance that sample catches were sufficiently large to provide accurate weighings and analyses. The three-sampler sites had one unit upwind (approximately 20 meters) and two units downwind (approximately 10 and 50 meters, depending on the site and sample catch). The two downwind samplers were approximately on the downwind axis.

Records of mine and plant activity were kept by the field crew for each sampling site. In particular, mining activities, blasting, haul truck operations, and crushing operations were logged, since all of these activities were intermittent or variable. This information was recorded on the same data sheets as the high-volume unit records.

Filters were removed from the high-volume samplers and cascade impactors after each test and sealed in polyethylene bags. The bags were placed in an envelope, with the location and field data recorded on the envelope. The basic record number for each sample was the filter sequence number, which was printed on each filter. Therefore, the results associated with each sample were directly traceable back to the filters, which were put into storage unless they were consumed in a subsequent analysis step.

As already noted, the key to assuring continued operation of both high-volume samplers and meteorological instrumentation was close surveillance by the field crew. The air flow rate through the high-volume units was recorded from rotometers at the beginning and end of each sample collection. Local temperatures and pressures were recorded to correct the average actual flow rates to standard conditions. The rotometers were calibrated against a calibrated orifice meter at the start of the field testing program.

Total suspended particulate (TSP) values were determined for each sample collected from stabilized filter weights, sample time, and corrected sampler air flow rate. Before-and-after weights were taken under controlled temperature and humidity conditions. The cascade impactor filters were weighed under controlled conditions as well, and particulate size breakdown determined from impactor calibration curves, down to about the 0.5μ (and less) cutoff. A five-stage impactor was used. Fiberglas filters were used for TSP determinations and (in some cases) subsequent organic analysis. Figerglas filters have excellent weight stability, since water absorption is negligible. Since Fiberglas filters cannot be decontaminated well enough for good elemental analysis, Whatman paper filters were used for inorganic determinations. There is a trade-off involved in this choice, since paper filters are difficult to stabilize and the resulting net sample weights are probably less accurate than samples collected on Fiberglas.

Organic analyses require large (1 to 10 g) samples to be quantitative, especially for spent shale (which has the lowest organic content). Therefore, the sampling time for organic analysis samples was considerably longer than other samples. In some cases with a 24-hour source operation, the high-volume units were run overnight to collect a sufficient sample mass. Locating a sampler within a few meters of the dust source was another technique used to increase sample size.

Meteorological data were recorded on strip charts, and average conditions were manually interpreted for each hour of operation. Wind direction and air temperature were directly recorded, while average wind speed was calculated from the "wind run" trace (which is an integrated wind speed).

The final quality assurance step was data validation by comparison with similar samples. The size of the data base obtained from the test program was large enough to allow these comparisons to be useful. In some cases, for example, the appearance of insufficient sample size was confirmed by gross variances in analytical results. Accuracy estimates for analysis methods were used to determine the statistical validity of analytical results.

Offgas Sampling Execution

Gas samples for field analysis were taken using an integrated gas sampling train. Samples were drawn through a stainless steel probe to an ice bath condenser by means of a small diaphragm pump, and then metered into a Tedlar bag. At the conclusion of the sampling, the bag was sealed and transported to a mobile lab for analysis of inorganics (CO_2, O_2, N_2, CO, SO_2, NO_x) and light hydrocarbons (C_1-C_6).

Standard EPA absorption train methods (Figure 6) were used for some sulfur-based constituents (H_2S, SO_2, SO_3). Other constituents for which selective absorption was attempted included NH_3, arsenic, and mercury. Total sample volumes for the various tests ranged from 0.02 to 0.2 cubic meters at 20°C.

The particulate matter in the gas discharge after passing through a thermal oxidizer was captured with a high volume (0.1 std cu meters/min) Source Assessment Sampling System (SASS), shown schematically in Figure 7.

About 12,000 standard liters of sample gas were processed in each test, allowing higher accuracy than found in traditional low volume sampling equipment. Traverses and gas velocity measurements across the stack were done in conformance with standard stack sampling procedures.[2]

The probe assembly used for recycle gas collection (for subsequent analysis in the C_6-C_{12} range) is shown in Figure 8. The sample collection procedures used multiple methods, including evacuated gas bottles, cold trap tubes, and polymeric adsorbents.

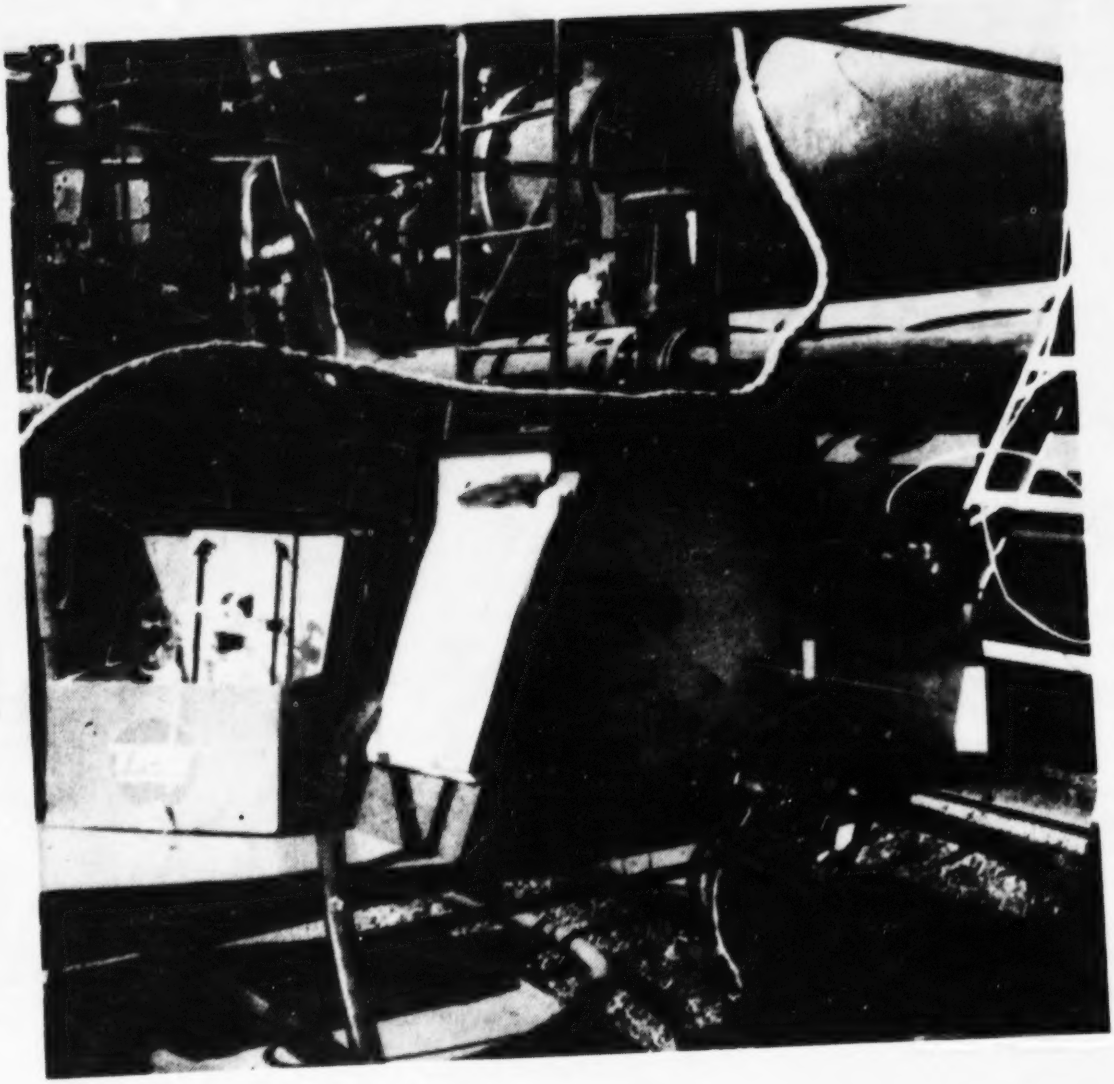


Figure 6. Absorption Train at Recycle Gas Sample Location.

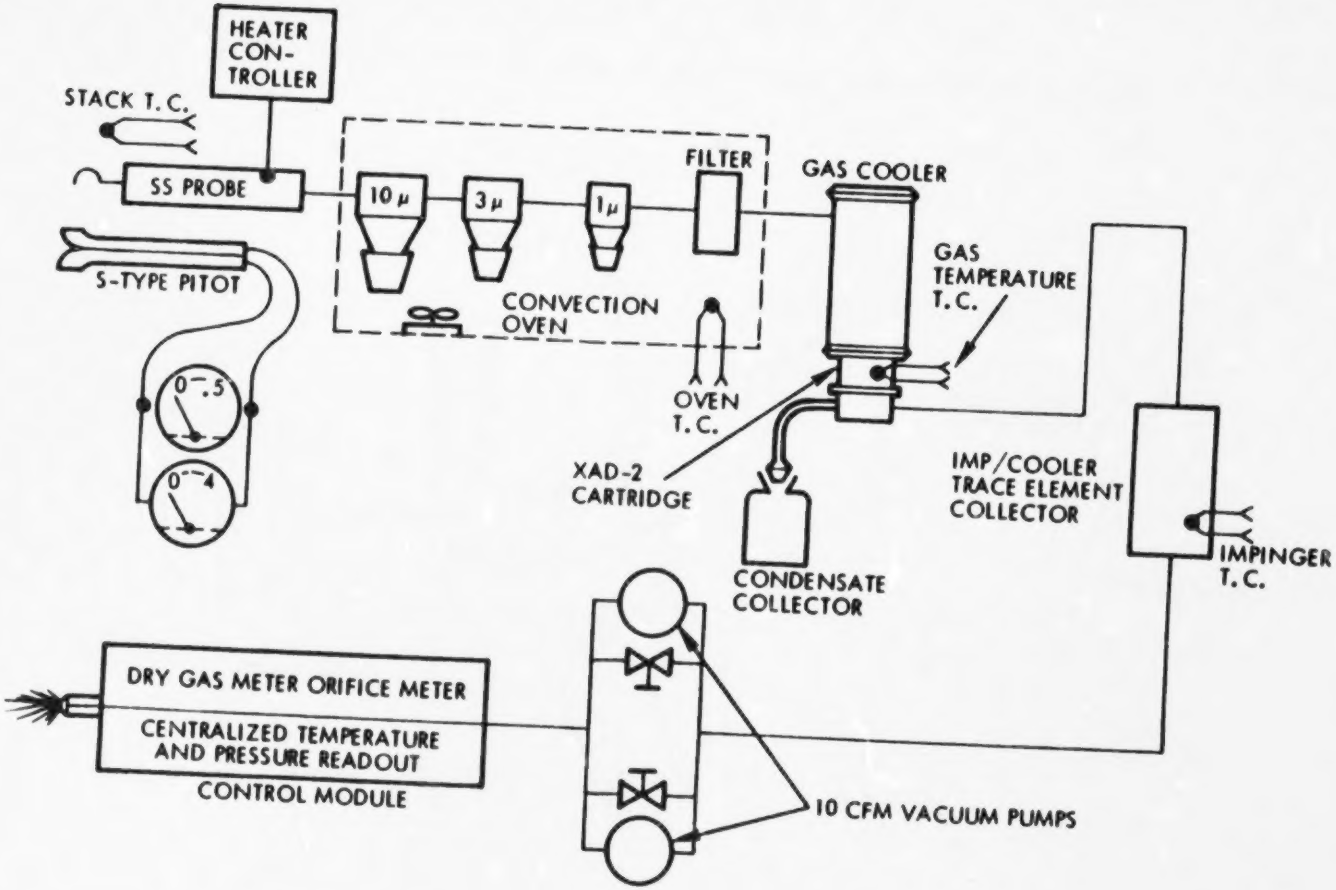


Figure 7. SASS Train Schematic.

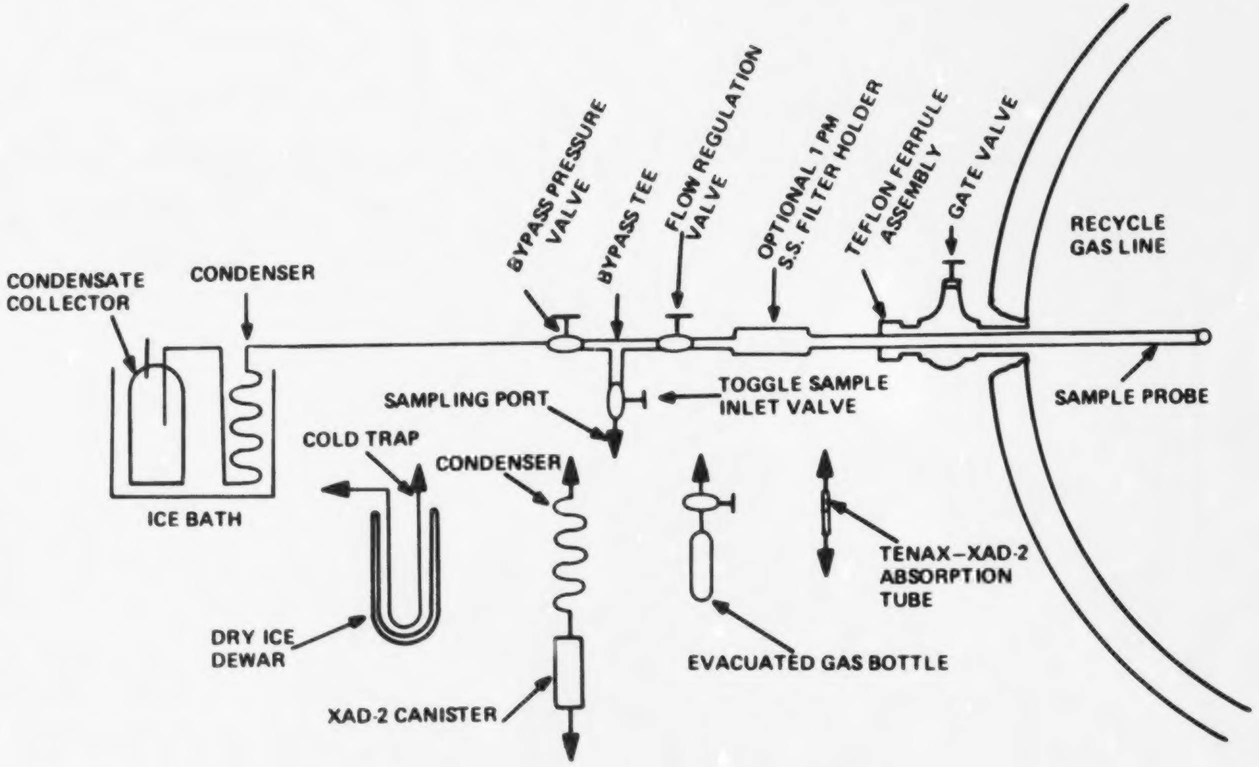


Figure 8. Schematic Diagram of Recycle Gas Sample Probe Assembly.

Impinger solutions used to collect H_2S, SO_2, and NH_3 were analyzed by standardized wet chemistry methods, while Hg was determined by atomic absorption spectroscopy (AA). Arsenic (as arsine) was sought by AA methods as well, but the collected quantities were apparently below the level of AA detection. Another analysis effort was undertaken, using a reducing agent ($NaBH_4$), separation and identification. This latter technique was successful, with a quantitation limit of 10 ng for arsine.

Laboratory analysis for C_6 through C_{12} hydrocarbons consisted entirely of separation with a gas chromatograph, coupled to a mass spectrometer for constituent identification. Quantification of 53 compounds was then accomplished by gas chromatography. The GC/MS identification procedure required a concentrated sample, provided by the cold-trap samples. Duplicate gas bottle samples were injected in triplicate for GC quantification. Eight standard gases were used for GC column calibration, as well as verification of the mass spectrometer identification.

RESULTS

Results and Discussion of Fugitive Dust Measurements

Total suspended particulate (TSP) measurements of fugitive dust can be effectively carried out with high-volume samplers in the vicinity of oil shale mining and handling operations. Measurements conducted at the Anvil Points mine adits appeared to be the most definable, since fugitive dusts from mining, blasting, and vehicular exhausts were confined. Measurements in open areas (haul road, retorted shale transfer, crushing) will vary considerably from one high-volume sampler to the next, implying that a single sample source cannot supply data which is typical for the area. A number of samplers must be used, to allow for random variations in dust concentrations under varying wind and terrain conditions. The sampler configuration used in this study (two-downwind, one-upwind) is probably a minimum choice to provide useable TSP statistics.

TSP data included in this work appeared to be credible with sample volumes as low as 30 cubic meters, while sample volumes of 15 cubic meters tended to give results that were out of line with larger sample volumes. Although the data are useful measures of ambient dust concentrations at ground level, they are too scattered or biased to be used for very accurate dispersion or source emission estimates. TSP trends over the course of a number of days are indicated in Figure 9 for the retorted shale handling area, with sampler positions indicated by distance upwind (N) or downwind (S). Consistently higher concentrations were measured at 35 meters downwind than at 15 and 20 meters downwind of the source. The only other apparent contributor of dust in the vicinity was the crushing and screening operations which were always downwind of the samplers during the testing periods. A possible explanation of this result is that the samplers at 15-20 meters, having been placed in a lower elevation that the source, were missing a portion of the centerline dust concentrations. The samplers at 35 meters were at about the same elevation as the source, since the terrain was rising at this point. Although there is considerable scatter in these measurements, it is clear that increased TSP values will be observed in the immediate vicinity of handling operations. When the Figure 9 TSP values at each downwind distance (x) are averaged, a best-fit regression curve of the form TSP = 11.34 x -0.27 appears to be a good prediction for observed dust concentration.[3] Increased dust levels were observed in Figure 10 as a result of mining activities, especially blasting on 9/27.

The use of slotted-plate cascade impactors for particle sizing has become reasonably common with high-volume sampler usage. The four-stage-plus-backup filter version used in this study had an expected particle size cutoff pattern (at 50% collection efficiency) as follows:

Stage	1	2	3	4	5
50% cutoff (microns)	7.2	3.0	1.5	0.95	0.49

An examination of the data averages for particle size distributions showed an apparent bimodal distribution, with 30 to 50% of the total sample catch appearing on the backup filter. If the mass of particulate on the backup filter is treated as though it really is less than 0.49 microns in diameter, calculated mass median diameters will be less than typical urban suspended particulates. This conculsion is clearly invalid, and an optical scanning analysis of randomly selected backup filters was conducted to provide a limited QA audit of the extent of particle sizing inefficiencies. These results are given in Table 2, together with an estimate of the corrections in observed mass distributions when the particles counted on the filters are assumed to be spherical and unity density. The number of particles in each size range are reported as No. %, and on three of the four filters, particles in the 0-1 micron range were numerically in the minority.

TABLE 2. OPTICAL SIZING OF SELECTED FILTERS FROM PARTICULATE SEPARATION TESTS

Sample location		0-1.0μ	1.0-2.0μ	2.0-3.0μ	3.0-8.0μ	> 8.0μ
Retorted shale transfer	No. %	21.78	18.05	14.61	36.10	9.46
	Wt. %	0.02	0.35	1.32	34.83	63.47
Haul road	No. %	16.21	19.88	13.46	35.47	14.98
	Wt. %	0.01	0.29	0.89	25.08	73.73
Crusher area	No. %	19.25	17.08	10.56	40.37	12.73
	Wt. %	0.01	0.27	0.76	30.98	67.98
Mine adit No. 1	No. %	72.85	8.61	2.65	10.93	4.97
	Wt. %	0.12	0.38	0.54	23.77	75.19

(Polarized light microscopy performed by Walter C. McCrone Associates)

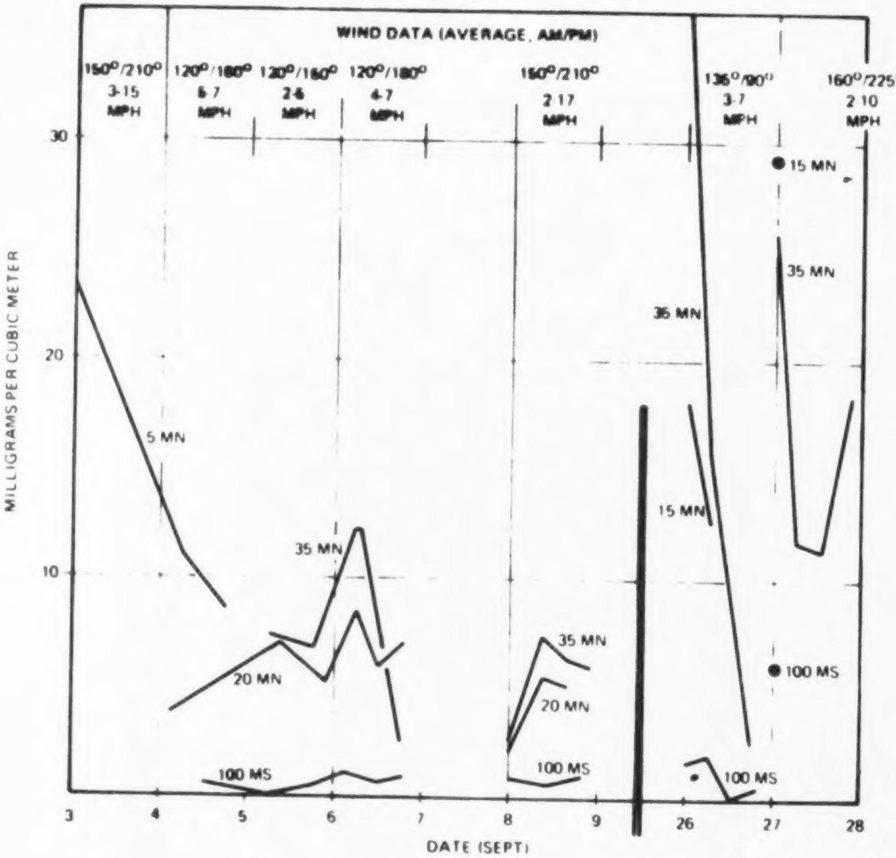


Figure 9. TSP Values for Retorted Shale Transfer Area.

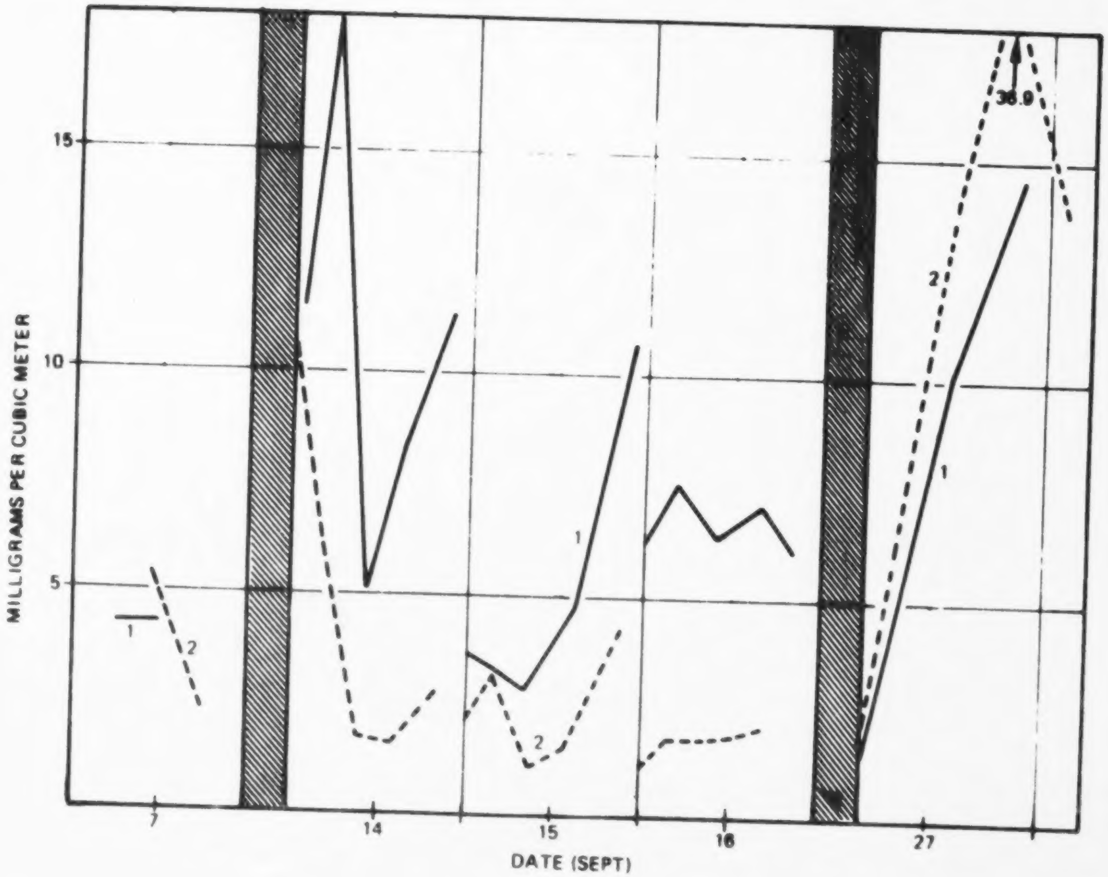


Figure 10. TSP Values for Mine Adits 1 and 2.

We believe that the trend of particle size distributions on the selected high-volume filters summarized in Table 2 provides convincing evidence that the cascade impactor separation was subject to a great deal of particle bounce error. Particles larger than 3 microns dominate the weight percentage on these filters, and the range that the filters were intended to catch (0-1 microns) represent a negligible weight percentage. Even 5% of the number of particles being in the over 8 micron category (as in the mine adit sample) will seriously bias the mass distributions.

Organic and inorganic analysis results from these dust samples are reported elsewhere.[4] As part of this analysis effort, it was noted that infrared scans of organic extracts were partially masked by the presence of silicon oils, and that the Fiberglas filters were the source of the contamination. Solvent extraction of the filters prior to use was recommended as a future quality assurance requirement for samples intended for organic analysis.

Results and Discussion of Offgas Measurements

Instrumental analysis of recycle and thermal oxidizer gases has been demonstrated to be a reliable method, using grab-bag sampling methods, for both light hydrocarbons and combusion gases. Where concentrated gas stream constituents were required (e.g., volatile trace elements), capture in sample train impinger solutions was the method of choice. The proper selection and sequence of impinger solutions depends on a semiquantitative knowledge of the constituents in the gas stream. Capture of heavier organics (C_6-C_{12}) was feasible with evacuated gas bottles and cold-trap tubes, but adsorption on polymeric materials still appears to be a technique that should be investigated for applications to shale oil processing streams. High-volume particulate sampling trains (SASS trains) were needed to get repeatable results from the thermal oxidizer discharge.

The standard analysis methods used for typical waste gas stream constituents (H_2S, SO_2, NH_3) appear to be reliable procedures that can be done within reasonable variance ranges, but instrumental analysis for SO_2 and NO_x is easier and faster. Results for these constituents were consistent with measurements made at Paraho during 1976. Ammonia was found in the recycle gas stream at about 1 volume percent levels, along with hydrogen sulfide (in the 0.1 volume percent range). These constituents would be removed in a gas-cleaning unit under full-scale operations. Emissions from burning the treated gas would then be similar to natural gas combusion.

The volatile trace elements mercury and arscenic were detected. The detection of arsenic provides some extremely useful information for Paraho gas streams, because the very small amounts found (> ppb) suggest that removal will not be required.

CONCLUSIONS

The quality assurance planning involved in the fugitive dust and offgas survey has allowed subsequent analysis and data interpretation to be carried out with a maximum utilization of the effort involved in a month-long field sampling program. Pretest determinations of minimum sample sizes, reagent requirements, contamination prevention, and sample identification procedures are all essential. The audit role of quality assurance cannot be underemphasized either. Two highlights of the QA audit effort in this program were the detection of probable errors in fugitive dust particle size determination by cascade impactors, and the idenfication of trace organic contamination of Fiberglas filters from silicon oils. Both of these evaluations were made with the aid of alternative measurement methods that would not have been used for a large number of samples.

A definite conclusion reached from this work is that fugitive dust particle sizing with cascade impactors should be calibrated with optical sizing techniques, and that the first stage of an impactor should be preceded by a cyclone collector with about a 5-micron cutoff. These procedures should compensate for the particle bounce problem by preventing most of the 5-micron and heavier particles from reaching stages with a lower cutoff, and by assessing the bias introduced by particle bounce in the size ranges under 5-microns.

Offgas measurements should be made with continuous monitors whenever possible. GC/MS analysis of gas samples for trace organics is a very effective technique. Although trace element analysis of gas samples was successfully done in this program, further research will be needed to develop continuous monitors for this purpose.

ACKNOWLEDGEMENTS

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INTERCOMPARISON STUDY OF ELEMENTAL ABUNDANCES IN RAW AND SPENT OIL SHALES

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INTRODUCTION

Techniques for accurate and sensitive elemental analysis of oil shale materials are important for determining the fate and effects of various constituents during oil shale conversion. Many routine analytical techniques are not suitable for oil shale materials due to numerous chemical interferences.[1-3] The need for oil shale reference standards was first recognized by Poulson et al.[2]

The purpose of this work was to develop raw and spent oil shale reference samples, to characterize them using an interlaboratory, interinstrumental approach, and to assess the performance of various analytical methods. This study was jointly carried out using the analytical facilities of various Colorado universities (COLO), Battelle Pacific Northwest Laboratory (PNL), the Lawrence Berkeley Laboratory (LBL), and the Lawrence Livermore Laboratory (LLL). Analytical procedures routinely used at those laboratories for similar measurements on other geochemical materials were used. Thus, some laboratories analyzed a single sample rather than several replicates.

Aliquots of the reference standards described in this work may be obtained by writing the authors.

EXPERIMENTAL

Instrumental neutron activation analysis (INAA), X-ray fluorescence spectrometry (XRF), atomic abosrption spectroscopy (AA), emission spectroscopy (ES), gamma-ray spectrometry (GS), and colorimetric and fluorimetric methods were used to measure 52 elements in four oil shale reference samples. Preparation of the reference samples and analytical procedures used by the participating laboratories are described. Measurements by the Colorado universities were made under the auspices of the Colorado Environmental Trace Substances Research Program which consists of a number of research groups at various Colorado universities. There is no central laboratory--reported measurements were made at the Colorado School of Mines, the University of Colorado, or Colorado State University. The U.S. Geological Survey neutron activation and delayed neutron analyses were performed on a service basis for the Colorado universities group for this study.

Reference Samples

Four reference samples were prepared for this study. Samples OS-1 and FASS were prepared at the Colorado School of Mines using procedures previously described.[3,4] Sample OS-1 is a raw oil shale from the Dow Mine, Colorado. Twenty-seven kilograms of material were prepared by crushing and grinding to -65 mesh and blending and splitting into 75-g samples. FASS is Fischer Assay spent shale produced by 46 repetitive runs of Fischer Assay retorts charged with OS-1.[3]

Samples RAW-1B and SOS-11B were prepared at the Lawrence Berkeley Laboratory using procedures described here. RAW-1B is a raw oil shale from the Anvil Points Mine, Colorado; SOS-11B is a spent shale produced during a high-temperature combusion run of the Lawrence Livermore Laboratory's 125-kg simulated *in situ* retort.[5]

RAW-1B was prepared from master batch material received from Lawrence Livermore Laboratory (LLL). The master batch material was prepared by LLL by separating 136,000 kg of Anvil Points oil shale into greater-than and less-than-102-mm fractions with a grizzly; passing the less-than 102-mm material through a roll crusher; and screening the material to the size range of 13 mm to 25 mm. A 25-kg sample of the 13-mm to 25-mm material was split from the master batch and mixed and split into 500-g lots, using the technique described by Wildeman.[4] Random number tables were used to select two lots. Selected lots were ground to less than 3 mm in an alumina-faced jaw crusher, and to less than 0.15 mm, with most passing 0.074 mm in an alumina-jaw pulverizer; they were then split into 15-g samples for use in this work. The 15-g samples were stored in acid-washed glass vials and maintained at 4°C.

SOS-11B was prepared by grinding the charge from the 125-kg retort in a Sturtevant rotary grinder with a built-in splitter. A 25-kg sample was split from the rotary-ground material and prepared for analysis as described for RAW-1B.

A minimum of three separate splits of each of the four standards was tested for homogeneity by measuring elemental abundances by neutron activation analysis and X-ray fluorescence spectrometry.[4] All samples were found to be homogeneous within the analytical precision of the method.

Neutron Activation Analysis

Battelle Pacific Northwest Laboratory -

Two procedures were used by PNL. The first procedure was used to analyze all four samples, and the second was used only for RAW-1B. In both procedures, 0.1 to 0.5 g of sample were weighed into 0.4-dram polyethylene vials; the vials were then heat sealed. The 0.4-dram vial was placed in a 2-dram polyethylene vial which was also heat sealed. After irradiation, the samples were transferred to fresh vials. Standards used for elemental analysis were Fischer atomic absorption standards for As, Ni, Zn, and Se; National Bureau of Standard's orchard leaves (SRM 1571); U.S. Geological Survey standard rocks BCR-1, W-1, AGV-1, and PCC-1; and IAEA standard Soil-5. Samples were irradiated at the Oregon State University reactor at a power of 1 MW.

Triplicates were analyzed in the first procedure and the reported errors are the larger of 1 standard deviation for the replicates, 1 standard deviation from the counting statistics, or 2% of the reported value. The analysis procedure used one irradiation period and two decay/counting intervals, as shown in Table 1. Following the irradiation, the samples were transferred into clean polyethylene vials and counted on an 80-cc Ge(Li) detector with a resolution of 1.96 keV at 12% relative efficiency after the 7-day cooling period. Counting following the 6-week cooling period was done on an anticoincidence-shielded Ge(Li) detector to reduce Compton background for low- and medium-energy gamma rays, and, in some cases, to remove peak interferences from correlated gammas.

A single aliquot of RAW-1B was analyzed by the second procedure; the reported errors are the larger of 1 standard deviation for the counting statistics of 2% of the reported value. The analysis procedure used one irradiation period and three decay/counting intervals. The samples were counted on a 130-cc Ge(Li) detector with a resolution of 1.8 keV at 25% relative efficiency following the 7-day and 30-day cooling periods. Counting following the 70-day cooling period was done on an anticoincidence-shielded Ge(Li) detector.

Lawrence Berkeley Laboratory -

Two replicates were analyzed. The reported error is an estimate of 1 standard deviation in the accuracy calculated from the counting statistics of both the samples and the standards and the uncertainties in the elemental abundances in the standards. The samples were analyzed using procedures similar to those described elsewhere.[6] Approximately 100 mg of sample were mixed with 50 mg of cellulose and compacted into a 1 cm x 1.2 mm pill using a hand-operated hydraulic press. The samples were wrapped in thin polyethylene and placed in radial array with four samples and five standards (standard pottery,[6] KCl, $CaCO_3$, and Al foil) in a heavy-duty polyethylene irradiation capsule. The sealed capsule was suspended by a wire in the central thimble of the Berkeley Triga Reactor and rotated during irradiation. The technique used to analyze the resulting pills consists of two irradiation periods and five decay/counting intervals, as summarized in Table 1. Three of these were made with a 7-cc intrinsic Ge detector with a resolution of 1.6 keV at 1 MeV and two were made with a 1-cc Ge(Li) detector with a resolution of 0.54 keV at 103 keV. For the second irradiation, the samples were rewrapped in high-purity Al foil and placed in radial array in an Al irradiation capsule.

Lawrence Livermore Laboratory -

A single sample was analyzed using an absolute INAA procedure described elsewhere.[7] Approximately 200 mg of sample were mixed with 200 mg of Avicel, pressed into a 1.59-cm-diameter disc, and stacked in an Al irradiation capsule between polyethylene spacers. Flux monitors consisting of U and Sc were placed at opposite ends of the tube. Following irradiation of the samples, the disc was removed from the outer vial and placed in a second container for counting. The analytical technique uses two irradiation periods and five decay/counting intervals, as summarized in Table 1. The samples were irradiated in the Livermore pool-type reactor which is moderated and cooled by light water and consists of plate-type fuel elements and boron-containing control rods. The samples were counted on 50- to 70-cc Ge(Li) detectors.

Colorado Universities -

Samples OS-1 and FASS were analyzed by the U.S. Geological Survey in Denver under contract to the Colorado School of Mines. The procedure used was similar to that described elsewhere.[8] Three replicates were analyzed. The reported errors are the larger of 1 standard deviation for the replicates or 2% of the reported value. Approximately 0.8 g of a powdered sample were weighed into 2-dram polyethylene vials and irradiated in the General Atomic TRIGA Mark I reactor. Standards used for the analysis were U.S. Geological Survey G-2 and two specially prepared combined quartz standards containing the elements of interest. The analysis procedure used two irradiation periods and four decay/counting intervals. Following the irradiation, the samples were transferred into clean polyethylene vials and counted on a 30-cc Ge(Li) detector with a resolution of 2.0 keV at 12% relative efficiency. A 10-min cooling period was used for the first irradiation. In addition to the high efficiency Ge(Li) detector, a low-energy intrinsic Ge detector with a 1-cc active volume and 0.48 keV resolution at 122 keV was used for the 7-, 14- and 60-day cooling periods.

X-ray Fluorescence Spectrometry

TABLE 1. NEUTRON IRRADIATION AND COUNTING SCHEDULES USED BY LBL, PNL, LLL, AND THE USGS

	Irradiation time	Neutron flux n/cm^2-sec	Cooling time	Counting time, min	Elements detected
LBL	18 min	2×10^{11}	8 min	1	Al, Ca, V, Cl, Mg, Ti
			1.25 hr	6	Mn, Na, K, Eu, Ba, Sr, Cu, In, Ga
	8 hr	2×10^{13}	6 days	20	U, Sm, Lu, Ti, La, As, Br, Cd, Mo, W, Ba, Au
			30 days	60,90	Fe, Sc, Ta, Eu, Zn, Co, Cs, Sb, Ce, Ir, Se, Ag, Hf, Th
PNL	2 hr	6×10^{12}	7 days	300	Na, La, Sm, As, Sb, Co, Fe, Rb, Sc, Ba, Hf
			6 weeks	300	Cr, Th, Eu, Sr, Ni, Rb, Zn, Se
	8 hr	6×10^{12}	7 days	100	Sm, Lu, Yb, Ba, La, Na, Br, As, K
			30 days	100	Fe, Cr, Th, Sb, Ce, Co, Hr, Hg, Rb, Sc, Ta, Yb
			70 days	1000	Eu, Sc, Zn, Ni, Sr, Se, Tb
LLL	2 min	2.1×10^{13}	10 min	10,20,40	Al, V, Cu, Ti, Ca, Na, Mg, Cl, Mn, Br, I, Ba, In, Dy, As, Ga, Sm, V, Mo
	72 min	2.6×10^{13}	3 days	133	Na, As, W, Ga, K, Cd, Mo, V, Sm, Au, Hg, La, Sb, Mo, Zn
			15 days	333	Fe, Cr, Co, Zn, Hg, Se, Ag, Sb, Ce, Cs, Eu, Sc, Th, Ni, Ta, Hf, Ba, Rb
USGS	20 min	2.5×10^{10}	10 min	20	Na, K, Ca, Mn, Sr, Ba, La, Dy
	8 hr	2.5×10^{12}	7 days	20	Ca, Cr, Ba, La, Ce, Nd, Sm, Eu, Yb, Ta, U
			14 days	33	Sc, Cr, Fe, Co, Zn, Rb, Sb, Ba, Ce, Nd, Eu, Tm, Lu, Hf, Ta, Th, U
			60 days	167	Sc, Cr, Fe, Co, Zn, Sa, Rb, Sr, Nb, Sb, Cs, Ce, Eu, Gd, Tm, Yb, Hf, Ta, Th

Battelle Pacific Northwest Laboratory -

Three replicates were analyzed. The reported errors are 1 standard deviation for the three analyses. The samples were analyzed using procedures similar to those described elsewhere.[9] Samples were prepared by pressing 0.250 g of powder and an equal weight of cellulose into a 3.2-cm-diameter disc. The samples were analyzed on a Kevex Model 810 energy-dispersive X-ray machine. System resolution was 200 eV at 6.4 keV (Fe Kα X-ray). Excitation was provided by a Zr or Ag secondary source. The X-ray tube was operated at 50 kV with a current of 35 mA. The resulting radiation was measured with a 80-mm^3 detector and a 1000-channel pulse height analyzer. Counting time was 100 minutes. The elements analyzed were Si, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Hg, Se, Pb, As, Br, Rb, U, Sr, Y, Zr, Nb, and Mo. Individual calibrations were calculated for each sample matrix from backscatter intensities and multi-element, thin-sample calibration curve.[9]

Lawrence Berkeley Laboratory-

Two energy-dispersive X-ray fluorescence systems were used. The "low-energy" system was used to analyze for Al, Si, Ti, Fe, Na, K, Ca, and Mg. Two replicates were analyzed. The reported errors are the larger of 10% of the reported values, or 1 standard deviation for the counting statistics. The samples were prepared using a $LiBO_2$ fusion technique.[10] Approximately 200 mg of powdered sample were fused with 1.80 g of $LiBO_2$ in a Pt crucible over a Fischer burner. The temperature of the mixture was slowly raised to 900°C, the mixture was poured into an Al ring, which was resting on a vitreous carbon disc at 250°C, and pressed into a ring with a hydraulic press. Weight loss on fusion was measured and used to compute elemental abundances. The samples were analyzed using a prototype energy-dispersive system designed and built at LBL.[10] The samples were placed in a vacuum chamber maintained at 10^{-4} torr or better and irradiated with a multiple anode soft X-ray generator consisting of six anodes and an electron gun. Emitted radiation was measured using a lithium-drifted silicon detector and a multichannel analyzer.

The "high-energy" system was used to measure the elements Ti and heavier which have X-ray energies >4.5 keV. Two replicates were analyzed. The reported errors are the larger of 1 standard deviation for the two analyses, 2 standard deviations from the counting statistics, or 4% of the reported value. The samples were analyzed using procedures similar to those described elsewhere.[11] Approximately 2 g of powder were pressed into a Lucite cylinder and analyzed on a prototype system designed and built at LBL. The total system resolution FWHM was 190 eV at 6.4 keV (Fe Kα X-ray) at 5,000 counts/sec using 18 μsec pulse peaking time. Excitation was provided by a Mo X-ray tube with external Mo filters. The X-ray tube was operated at 45 kV and with regulated currents that varied from 100 to 245 μA. The resulting X-rays were simultaneously measured by a guard-ring detector with pulsed-light feedback electronics and 512-channel pulse height analyzer. Counting time was 20 minutes.

University of Colorado -

Six to eight replicates were analyzed. The reported errors are 1 standard deviation for the replicates. Samples were prepared and analyzed (by a procedure described elsewhere)[12,13] by glueing 250 μg of powdered sample into the center of a Forvar foil. The samples were analyzed on a prototype system built at the University of Colorado cyclotron facility. Excitation was provided by a 2-kW tungsten anode X-ray tube operated at 55 kV and with regulated currents varying from 2 to 20 mA. The total system resolution FWHM was 163 ev at 6.4 keV (Fe Kα X-ray). The resulting X-rays were measured on an 80-mm^2, lithium-drifted, silicon X-ray detector, arranged in a compact geometry, and a 512 channel pulse height analyzer. The counting time was not fixed but was normally about 2 hour. The configuration of the system was adjusted so that the background was lowest for the Mo Kα X-ray. This made the background under K, Ca, Ti, Cr, and Mn somewhat high and the uncertainties in the analysis of these elements is correspondingly larger. The data reduction method used peak areas, compared to thin-film, pure-element standards.[12,13]

Atomic Absorption Spectroscopy

Battelle Pacific Northwest Laboratory -

Atomic absorption spectroscopy was used to measure Al, Ca, Fe, Hg, K, Mg, Na, Si, Sr, and Ti. Conventional flame atomic absorption was used for all elements except Hg which was determined by flameless atomic absorption. Measurements were made with a Perkin Elmer 403. Powdered samples were fused with lithium metaborate using a 6:1 $LiBO_2$ sample ratio. The fused sample was dissolved in concentrated HNO_3 and diluted to 200 ml. Commercially prepared aqueous standards were used. USGS standard rock BCR-1 was used as a control.

Mercury was determined using a flameless technique. A 50 to 150-g sample was combusted, the vapors swept into a separation train, and the mercury trapped on gold beads and analyzed by flameless AA. In the separation train, mercury-free air was introduced into a 950°C quartz tube containing the sample overlying a layer of 3-4 cm of gold-coated quartz beads. The high temperature and oxidizing conditions volatilized the mercury from the sample matrix and the gold beads converted it to the elemental form. Elemental mercury was separated from interfering organic vapors by passing the sample gases through an alumina column which selectively retains the organic vapors but passes Hg^o. The Hg^o was collected by amalgamation in a column of gold-coated glass beads maintained at room temperature. This column was detached from the separation train and attached to a flameless AA system. Amalgamated Hg^o was released by heating the column to 500°C in a N_2 gas stream. The Hg^o vapor was swept into a long-path-length gas absorption cell where it was measured by atomic absorption at 254 nm.

Lawrence Berkeley Laboratory -

Zeeman atomic absorption spectroscopy was used to measure Cd, Hg, Cu, Pb, and Zn. The reported error is the larger of 10% of the reported value or 1 standard deviation for three replicates. The instrumental technique has been described elsewhere.[14-18] Electrodeless discharge lamps were used for all elements. Mercury was atomized in a T-shaped combustion tube maintained at 900°C and Cd, Pb, and Zn, were atomized in a Massman-type furnace equipped with a dual chamber graphite rod.[16] Powdered samples for Pb, Zn, and Cd analysis were diluted with graphite powder (Ultra Carbon U.C.P.-2-325) and mixed with a Wig-l-Bug. For the Hg analyses, the sample was directly weighed into a tared Pt boat and inserted into the furnace. For the other elements, the sample was weighed in a tared plastic tip for use with an adjustable micropipette and transferred to a Massman-type furnace by tapping the sides of the tip. The empty tip was weighed to determine transfer efficiency.

Colorado Universities -

Abomic absorption spectroscopy was used to measure Al, As, Ca, Mg, Si, and Na. Sample preparation consisted of standard HF, HNO_3, and $HClO_4$ digestions for Na, Mg, Al, Si, and Ca[19] and a sodium peroxide fusion for As.[3] The solids were spiked prior to digestion and standard additions used to check the analyses. Four replicates were analyzed for Al, Ca, Na, and Mg using standard flame conditions, and three replicates were analyzed for As using the hydride generation method.[3]

Emission Spectroscopy

Battelle Pacific Northwest Laboratory used a dc plasma technique to measure B. Three replicates were analyzed. The reported errors are 1 standard deviation for the three replicates. Samples were prepared by fusing 3 g of sodium carbonate with a 0.5-g sample, dissolving the residue in 8 M HNO_3, and diluting to 100 ml. The samples were analyzed on a Spectrametrics Spectraspan III employing a dc argon plasma excitation system and an Eschelle grating spectrometer.

Molecular Absorption

The Colorado universities used molecular absorption of AlF in an air-acetylene flame to determine F in a fused sample.[4] The analytical method was developed by Tsunada, Fujiwara, and Fuwa,[20] and was modified for oil shales by Meglen and Krikos.[21]

Gamma-Ray Spectrometry

The Lawrence Berkeley Laboratory used gamma-ray spectrometry to measure U, Th, and K.[22] Approximately 50 g of powdered sample were packaged in a 3.8-cm-diameter plastic container and counted for 1,490 to 3,829 minutes in a lead-shielded compartment with a 20-cm-diameter by 10-cm-thick NaI(Tl) crystal. The spectra were taken by a 1600-channel pulse-height analyzer covering the interval 0.1 to 4.0 MeV, and reduced by a computer program that fits, channel-by-channel, standard and sample spectra over selected energy intervals.

Fluorimetric and Colorimetric Methods

The Colorado universities used these techniques to measure Si, Se, Mo, and B. Silicon was determined colorimetrically by the standard molybdenum blue procedure.[23] Selenium was determined by a fluorimetric method which uses 2, 3-diaminonaphthalene.[24] Molybdenum was determined colorimetrically using potassium thiocyanate[25] and B was determined using an Azomethine-H method.[26] The fusions and digestions used with these procedures have been previously described.[3]

Delayed Neutron

The U.S. Geological Survey determined U under contract to Colorado School of Mines by this technique. Approximately 10 g of powdered sample were analyzed by procedures given by Stuckless et al.[27]

RESULTS

Analytical results for the four samples are summarized in Tables 2 through 5. The data are grouped by analytical technique so that the performance of each method may be readily assessed. The data in Tables 2 to 5 were reduced using statistical techniques; the results are plotted in Figures 1 through 4. A minimum handling error of 2% was assigned to all values with unrealistically small errors. This is frequently a problem in neutron activation work when the analyst reports counting errors.

The error-weighted average ($\overline{X}$) was computed and the value

$$Z_i = \frac{X_i - \overline{X}}{\sigma_i}$$

was determined for each point, where X_i is the ith measurement of an element and σ_i is the associated standard deviation. Chauvenet's criterion[28] was applied to the largest Z_i for each element set for $N \geqq 2$ where N is the total number of measurements for a given element. A value was rejected if

$$Z_i \geqq P$$

where P was a 1/3 N probability function based on the normal curve of error. If a value was rejected, N was reduced by 1 and a new error-weighted average was computed. This procedure was applied only once per element for each sample. Finally, the percent deviation from the mean was computed for each value in an element set as

$$\%DEV = 100 \frac{X_i - \overline{X}}{\overline{X}}$$

and the percent root-mean-square deviation for the element set determined as

$$\%RMS = 100\left[\sum_{i=1}^{N}\left[\frac{X_i - \overline{X}}{\overline{X}}\right]^2 N^{-1}\right]^{1/2}$$

The results of applying this procedure to the data developed in this study are shown in the last column in Tables 2 to 5 and by Figures 1 to 4. The last column of each table summarizes the error-weighted average obtained for each sample after applying Chauvenet's criterion[28] and the number of separate determinations included in the average. Application of this criterion resulted in the rejection of 12 values for SOS-11B, 16 values for OS-1, 21 values for FASS, and 19 values for RAW-1B. The errors reported in the last column are the larger of the error-weighted standard deviation of the laboratory values included in the average, or the smallest reported error of the individual laboratory values included in the average.

Figures 1 through 4 summarize the %RMS deviation, %DEV, and the coefficient of variation for each technique in an element set. The %RMS deviation is recorded along the top of each graph and is a measure of the uncertainty in the determination of the reported means for an element set. The %RMS deviation ranged from 0.0 to 22.2 in this study, with 85% of the values falling below 10%. The %DEV is plotted for each technique and is indicated by a geometrical symbol that designates the technique. The corresponding error bars are the percent standard deviation for each technique.

One interesting feature of this type of plot is that since an error-weighted average was used, the points will not necessarily distribute symmetrically about zero. This is particularly the case if a single point with a very small error dominates the average. Thus, a careful error analysis is critical. This is particularly serious for a small number of points. These problems have been partially alleviated by assigning a minimum analytical error of 2% to all points, and by evaluating the %RMS deviation. An analysis of this type assumes a normal distribution of errors. In some cases, such as in the reported results for arsenic, there may be a bimodal distribution caused by a systematic difference between methods. If the cause of the discrepancy was known, or at least suspected, the offending datum was rejected. Otherwise, the values were retained. One such example, involved a large fission product interference in the INAA analysis of Zr.

DISCUSSION

The results of this study show that most elements studied here can be reliably and accurately determined in raw and spent oil shales if careful

Table 2. ELEMENTAL COMPOSITION OF ANVIL POINTS RAW OIL SHALE PREPARED BY LBL, RAW 1B (ppm)

	Neutron Activation Analysis				X-ray Fluorescence Spectrometry				Other			Average		
	(A-1)	(A-2)	(B)	(C)	High energy (A)	High energy (B)	High energy (D)	Low energy (B)	(A)	(B)	(D)	Conc	No. of Values	
Al (%)	-	-	3.83±0.12	4.04±0.19	-	-	-	4.0±0.2	3.88±0.34[a]	-	-	3.93±0.12	(4)	Al
As	54±1	62±1	45±4	39±1	38±3	37±1	40±9	-	-	-	33±3[a]	42±1	(7)	As
B	-	-	-	-	-	-	-	-	108±11[g]	-	-	108±11	(1)	B
Ba	540±50	-	498±26	479±19	-	-	520±36	-	-	-	-	495±19	(4)	Ba
Br	0.52±0.16	-	-	-	-	<1.5	0.55±0.01	-	-	-	-	0.55±0.01	(2)	Br
Ca (%)	8.25±0.6	-	10.3±0.5	9.41±0.19	10.5±0.8	-	11±1	9.2±0.5	10.0±0.5[a]	-	-	9.6±0.2	(6)	Ca
Cd	-	-	-	-	-	-	-	-	-	0.72±0.07[b]	-	0.72±0.07	(1)	Cd
Ce	46±2	-	44±2	41.2±0.8	-	-	-	-	-	-	-	42±1	(2)	Ce
Cl	-	-	<830	-	-	-	-	-	-	-	-	<830	(1)	Cl
Co	9.3±0.3	8.8±0.2	9.18±0.29	8.56±0.17	-	<31	-	-	-	-	-	8.8±0.2	(4)	Co
Cr	45±1	49±1	37±2	33.1±0.8	-	-	-	-	-	-	-	46±1	(3)	Cr
Cs	-	-	4.46±0.33	4.40±0.10	-	-	-	-	-	-	-	4.41±0.10	(2)	Cs
Cu	-	-	-	<98	43±4	40±3	34±3	-	-	40±4[b]	-	39±3	(3)	Cu
Dy	-	-	2.48±0.13	2.13±0.14	-	-	-	-	-	-	-	2.32±0.13	(2)	Dy
Eu	-	0.59±0.03	0.63±0.02	0.59±0.01	-	-	-	-	-	-	-	0.60±0.01	(3)	Eu
F	-	-	-	-	-	-	-	-	-	-	990±20[a]	990±20	(1)	F
Fe (%)	2.41±0.05	2.29±0.05	2.21±0.06	2.16±0.04	2.2±0.2	2.18±0.09	2.10±0.04	2.1±0.1	2.24±0.31[a]	-	-	2.18±0.04	(8)	Fe
Ga	-	-	-	-	10.1±1.2	9.8±1.8	6.5±0.7	-	-	-	-	10±1	(3)	Ga
Ge	-	-	-	-	-	<2.4	-	-	-	-	-	<2.4	(1)	Ge
Hf	1.7±0.1	-	1.72±0.14	1.68±0.04	-	-	-	-	-	-	-	1.68±0.04	(3)	Hf
Hg	0.06±0.01	-	-	-	-	<4	-	-	0.086±0.005[a]	0.077±0.008[b]	-	0.083±0.004	(2)	Hg
In	-	-	<0.18	-	-	-	-	-	-	-	-	<0.18	(1)	In
Ir	-	-	<0.01	-	-	-	-	-	-	-	-	<0.01	(1)	Ir
K (%)	1.83±0.19	-	1.79±0.14	1.77±0.06	1.67±0.12	-	-	1.7±0.1	1.61±0.11[a]	-	-	1.73±0.04	(6)	K
La	21.2±0.5	20.2±0.4	20.8±0.7	23.4±0.3	-	-	-	-	-	-	-	20.6±0.4	(3)	La
Lu	0.26±0.03	-	0.19±0.01	0.214±0.008	-	-	-	-	-	-	-	0.21±0.01	(2)	Lu
Mg (%)	-	-	3.5±1.6	3.6±0.09	-	-	-	3.5±0.2	3.52±0.10[a]	-	-	3.6±0.1	(4)	Mg
Mn	-	-	343±12	334±7	350±30	341±21	300±8	-	395±70[a]	-	-	337±6	(5)	Mn
Mo	-	-	20±2	19±1	21±2	-	20±2	-	-	-	19±2[c]	20±1	(5)	Mo
Na (%)	1.54±0.03	1.58±0.03	1.56±0.04	1.53±0.03	-	-	-	1.7±0.1	-	-	-	1.56±0.03	(5)	Na
Nb	-	-	-	-	-	-	5.7±0.1	-	-	-	-	5.7±0.1	(1)	Nb
Nd	-	-	19±4	14±3	-	-	-	-	-	-	-	16±3	(2)	Nd
Ni	25±2	26±1	21±4	<36	23±3	20±4	29±1	-	-	-	-	24±2	(5)	Ni
Pb	-	-	-	-	24.5±0.5	24±2	23±1	-	-	23±3[b]	-	24±0.5	(4)	Pb
Rb	76±5	74±1	85±8	74±3	79±6	74±2	82±1	-	-	-	-	75±2	(6)	Rb
Sb	2.0±0.1	1.99±0.10	2.1±0.1	1.90±0.07	-	-	-	-	-	-	-	1.98±0.07	(4)	Sb
Sc	6.8±0.1	7.0±0.1	6.47±0.20	5.93±0.05	-	-	-	-	-	-	-	6.8±0.1	(3)	Sc
Se	2.6±0.3	2.6±0.3	-	2.38±0.30	2.2±0.5	2.1±0.7	-	-	-	-	-	2.5±0.3	(5)	Se
Si (%)	-	-	-	-	15.0±1.0	-	-	15.0±0.8	14.9±1.2[a]	-	-	15.0±0.8	(3)	Si
Sm	3.6±0.1	3.5±0.1	3.08±0.12	3.19±0.07	-	-	-	-	-	-	-	3.25±0.07	(3)	Sm
Sr	840±50	740±40	-	683±29	-	698±19	798±4	-	720±60[a]	-	-	712±19	(5)	Sr
Ta	0.55±0.02	-	0.46±0.02	0.47±0.04	-	-	-	-	-	-	-	0.46±0.02	(2)	Ta
Tb	0.37±0.04	-	0.40±0.07	0.36±0.02	-	-	-	-	-	-	-	0.36±0.02	(3)	Tb
Th	7.0±0.1	7.0±0.2	6.70±0.26	6.18±0.07		6.8±1.7	-	-	-	-	-	6.95±0.10	(4)	Th
Ti (%)	-	-	0.16±0.05	0.17±0.03	0.17±0.03	0.18±0.02	-	0.16±0.01	0.17±0.03[a]	-	-	0.16±0.01	(6)	Ti
U	-	-	4.10±0.16	3.63±0.20	-	-	-	-	-	-	-	3.92±0.16	(2)	U
V	-	-	107±24	92±5	-	-	-	-	-	-	-	93±5	(2)	V
W	-	-	-	-	-	-	-	-	-	-	-	-	-	W
Y	-	-	-	-	12±2	13±1	12±1	-	-	-	-	12±1	(3)	Y
Yb	1.6±0.1	-	1.38±0.05	1.31±0.03	-	-	-	-	-	-	-	1.33±0.03	(2)	Yb
Zn	70±6	65±5	-	75±3	69±7	67±3	63±2	-	-	-	-	65±2	(5)	Zn
Zr	-	-	-	-	56±8	-	49±3	-	-	-	-	50±3	(3)	Zr

A = Battelle Pacific Northwest Laboratory, B = Lawrence Berkeley Laboratory, C = Lawrence Livermore Laboratory, D = University of Colorado
E = U. S. Geological Survey, a = atomic absorption spectroscopy, b = Zeeman atomic absorption spectroscopy, c = colorimetric,
d = fluorimetric, e = delayed neutron, f = gamma-ray spectrometry, g = emission spectroscopy

Table 3. ELEMENTAL COMPOSITION OF DOW MINE RAW OIL SHALE, OS-1 (ppm)

	Neutron Activation Analysis			X-Ray Fluorescence Spectrometry				Other			Average		
	(A)	(B)	(E)	High energy (A)	High energy (B)	High energy (D)	Low energy (B)	(A)	(B)	(D)	Conc	No. of Values	
Al	-	3.41±0.12	-	-	-	-	3.4±0.2	3.4±0.3^a	-	3.5±0.1^a	3.43±0.10	(4)	Al
As	77±2	77±6	-	65±5	65±3	64±6	-	-	-	75±6^a	75±2	(5)	As
B	-	-	-	-	-	-	-	77±8^g	-	110±25^c	80±8	(2)	B
Ba	-	1225±47	1410±60	-	-	-	-	-	-	-	1295±47	(2)	Ba
Br	-	-	-	-	<1.5	-	-	-	-	-	<1.5	(1)	Br
Ca (%)	-	10.1±0.5	-	10.3±0.7	-	7.9±1.3	9.0±0.4	9.9±0.5^a	-	7.3±0.7^a	9.6±0.4	(5)	Ca
Cd	-	-	-	-	-	-	-	-	1.05±0.11^b	-	1.05±0.11	(1)	Cd
Ce	-	36±2	34±2	-	-	-	-	-	-	-	35±2	(2)	Ce
Cl	-	<700	-	-	-	-	-	-	-	-	<700	(1)	Cl
Co	9.2±0.2	10.8±0.3	18±5	-	<30	-	-	-	-	-	9.7±0.2	(2)	Co
Cr	28±1	35±2	46±7	-	-	-	-	-	-	-	29±1	(2)	Cr
Cs	-	4.49±0.34	4.4±0.2	-	-	-	-	-	-	-	4.4±0.2	(2)	Cs
Cu	-	-	-	49±5	52±4	44±2	-	-	-	-	46±2	(3)	Cu
Dy	-	1.87±0.11	2.4±0.2	-	-	-	-	-	-	-	2.0±0.1	(2)	Dy
Eu	0.49±0.04	0.54±0.02	0.54±0.01	-	-	-	-	-	-	-	0.54±0.01	(3)	Eu
F	-	-	-	-	-	-	-	-	-	1020±100^a	1020±100	(1)	F
Fe (%)	1.87±0.04	1.89±0.06	1.87±0.04	1.95±0.31	1.88±0.07	1.5±0.2	1.8±0.1	1.94±0.31^a	-	-	1.87±0.04	(8)	Fe
Ga	-	-	-	8.7±1.1	8.1±0.2	3.7±0.4	-	-	-	-	8.1±0.2	(2)	Ga
Ge	-	-	-	-	2.8±1.6	-	-	-	-	-	2.8±1.6	(1)	Ge
Hf	-	1.44±0.12	1.45±0.03	-	-	-	-	-	-	-	1.45±0.03	(2)	Hf
Hg	-	-	-	-	-	-	-	0.14±0.007^a	0.16±0.02^b	-	0.14±0.01	(2)	Hg
In	-	<0.20	-	-	-	-	-	-	-	-	<0.20	(1)	In
Ir	-	<0.01	-	-	-	-	-	-	-	-	<0.01	(1)	Ir
K (%)	-	1.36±0.13	1.33±0.06	1.25±0.01	-	-	1.2±0.1	1.17±0.11^a	1.20±0.02^f	-	1.23±0.02	(6)	K
La	18.4±0.4	18.8±0.8	19±1	-	-	-	-	-	-	-	18.5±0.4	(3)	La
Lu	-	0.16±0.02	0.20±0.02	-	-	-	-	-	-	-	0.18±0.02	(2)	Lu
Mg (%)	-	2.3±1.1	-	-	-	-	2.6±0.1	2.60±0.1^a	-	2.7±0.2^a	2.6±0.1	(4)	Mg
Mn	-	275±9	272±14	262±22	258±26	196±16	-	290±70^a	-	-	272±9	(5)	Mn
Mo	-	32±4	-	27±2	-	29±2	-	-	-	26±2^c	28±2	(4)	Mo
Na (%)	1.31±0.03	1.40±0.04	1.47±0.06	-	-	-	1.4±0.1	1.46±0.2^a	-	1.54±0.04^a	1.36±0.03	(5)	Na
Nb	-	-	-	-	-	4.5±0.2	-	-	-	-	4.5±0.2	(1)	Nb
Nd	-	16±4	15±1	-	-	-	-	-	-	-	15±1	(2)	Nd
Ni	32±3	30±4	-	33±4	26±5	25±1	-	-	-	-	31±3	(4)	Ni
Pb	-	-	-	32±3	30±3	28±1	-	-	29±2^b	-	29±1	(4)	Pb
Rb	72±4	80±8	68±2	72±5	65±5	68±3	-	-	-	-	68±2	(6)	Rb
Sb	2.6±0.1	3.2±0.2	3.2±0.1	-	-	-	-	-	-	-	3.2±0.1	(2)	Sb
Sc	4.5±0.1	5.16±0.16	5.0±0.1	-	-	-	-	-	-	-	5.0±0.1	(2)	Sc
Se	4.2±0.3	-	-	4.6±0.6	4.1±1.0	-	-	-	-	3.5±0.2^d	4.3±0.3	(3)	Se
Si (%)	-	-	-	13.5±1.0	-	-	13.0±0.6	13.5±1.0^a	-	13.0±0.3^d	13.1±0.3	(4)	Si
Sm	3.0±0.4	2.49±0.11	2.7±0.1	-	-	-	-	-	-	-	2.6±0.1	(3)	Sm
Sr	653±40	-	650±40	-	595±23	620±12	-	660±60^a	-	-	620±12	(5)	Sr
Ta	-	0.39±0.02	-	-	-	-	-	-	-	-	0.39±0.02	(1)	Ta
Tb	-	0.28±0.05	0.33±0.03	-	-	-	-	-	-	-	0.32±0.03	(2)	Tb
Th	4.6±1.0	5.17±0.20	4.8±0.1	-	6.0±2.0	-	-	-	5.35±0.21^f	-	4.9±0.1	(5)	Th
Ti (%)	-	0.13±0.05	-	0.18±0.01	0.14±0.02	-	0.11±0.01	0.14±0.03^a	-	-	0.12±0.01	(4)	Ti
U	-	4.54±0.18	6.1±0.5	-	-	-	-	-	4.24±0.09^f	5.4±0.3^e	4.4±0.1	(4)	U
V	-	127±30	-	-	-	-	-	-	-	-	127±30	(1)	V
W	-	2.8±0.4	-	-	-	-	-	-	-	-	2.8±0.4	(1)	W
Y	-	-	-	8.2±1.0	7.8±1.6	8.3±0.4	-	-	-	-	8.3±0.4	(3)	Y
Yb	-	1.04±0.04	1.0±0.1	-	-	-	-	-	-	-	1.03±0.04	(2)	Yb
Zn	91±5	-	-	72±6	74±4	70±5	-	-	91±9^b	-	74±4	(4)	Zn
Zr	-	-	63±2	54±7	-	49±1	-	-	-	-	49±1	(2)	Zr

A = Battelle Pacific Northwest Laboratory, B = Lawrence Berkeley Laboratory, C = Lawrence Livermore Laboratory, D = University of Colorado, E = U. S. Geological Survey, a = atomic absorption spectroscopy, b = Zeeman atomic absorption spectroscopy, c = colorimetric, d = fluorimetric, e = delayed neutron, f = gamma-ray spectrometry, g = emission spectroscopy

Table 4. ELEMENTAL COMPOSITION OF SPENT OIL SHALE FROM RUN S-11 OF LLL'S 125-kg RETORT PREPARED BY LBL, SOS-11B (ppm)

	Neutron Activation Analysis			X-Ray Fluorescence Spectrometry				Other			Average		
	(A)	(B)	(C)	High energy (A)	High energy (B)	High energy (D)	Low energy (B)	(A)	(B)	(D)	Conc	No. of Values	
Al	-	5.81±0.18	5.86±0.12	5.68±0.3	-	-	5.6±0.3	-	-	-	5.81±0.12	(4)	Al
As	59±1	65±6	54±2	58±5	56±3	60±2	-	-	-	51±4[a]	58±1	(7)	As
B	-	-	-	-	-	-	-	140±15[g]	-	-	140±15	(1)	B
Ba	-	725±50	680±23	-	-	740±31	-	-	-	-	704±23	(3)	Ba
Br	-	-	-	-	<1.8	<1.6	-	-	-	-	<1.6	(1)	Br
Ca (%)	-	14.0±0.7	12.3±0.2	14.5±0.5	-	16±2	12.3±0.6	13.9±0.5[a]	-	-	12.7±0.2	(5)	Ca
Cd	-	-	-	-	-	-	-	-	0.77±0.08[b]	-	0.77±0.08	(1)	Cd
Ce	-	63±4	58.1±1.2	-	-	-	-	-	-	-	58.5±1.1	(2)	Ce
Cl	-	<1180	-	-	-	-	-	-	-	-	<1180	(1)	Cl
Co	11.8±0.2	12.6±0.4	11.9±0.2	11.8±0.2	<38	-	-	-	-	-	11.9±0.2	(4)	Co
Cr	50±2	60±3	50.4±1.0	-	-	-	-	-	-	-	50±1	(2)	Cr
Cs	-	6.96±0.52	6.89±0.14	-	-	-	-	-	-	-	6.89±0.14	(2)	Cs
Cu	-	-	<98	63±5	55±5	48±2	-	-	50±5[b]	-	49±2	(3)	Cu
Dy	-	3.65±0.52	3.22±0.22	-	-	-	-	-	-	-	3.46±0.20	(2)	Dy
Eu	0.86±0.03	0.93±0.04	0.86±0.02	-	-	-	-	-	-	-	0.87±0.02	(3)	Eu
F	-	-	-	-	-	-	-	-	-	980±60[a]	980±60	(1)	F
Fe (%)	3.28±0.02	3.09±0.09	3.03±0.06	3.19±0.22	3.22±0.12	3.2±0.2	2.9±0.2	3.15±0.31[a]	-	-	3.08±0.06	(7)	Fe
Ga	-	-	-	14.6±1.6	13±2	10.4±0.4	-	-	-	-	14.0±1.2	(2)	Ga
Ge	-	-	-	-	<2.1	-	-	-	-	-	<2.1	(1)	Ge
Hf	-	2.84±0.23	2.58±0.05	-	-	-	-	-	-	-	2.59±0.05	(2)	Hf
Hg	-	-	-	-	<4.5	-	-	<0.005[a]	<0.01[b]	-	<0.01	(1)	Hg
In	-	<0.31	-	-	-	-	-	-	-	-	<0.31	(1)	In
Ir	-	<0.01	-	-	-	-	-	-	-	-	<0.01	(1)	Ir
K (%)	-	2.66±0.24	2.55±0.10	2.35±0.17	-	-	2.5±0.1	2.39±0.19[a]	-	-	2.50±0.10	(5)	K
La	30.0±0.4	31.8±1.1	29.8±1.5	-	-	-	-	-	-	-	30.5±0.6	(3)	La
Lu	-	0.32±0.03	0.33±0.01	-	-	-	-	-	-	-	0.33±0.01	(2)	Lu
Mg (%)	-	4.9±1.2	5.2±0.1	4.97±0.10	-	-	4.7±0.2	-	-	-	5.04±0.10	(4)	Mg
Mn	-	482±16	478±10	507±40	481±37	459±48	-	495±40[a]	-	-	480±10	(6)	Mn
Mo	-	27±4	25±2	28±2	-	27±1	-	-	-	33±3[c]	27±1	(4)	Mo
Na (%)	2.41±0.05	2.45±0.07	2.41±0.05	-	-	-	2.4±0.1	-	-	-	2.42±0.05	(4)	Na
Nb	-	-	-	-	-	8.9±0.6	-	-	-	-	8.9±0.6	(1)	Nb
Nd	-	27±5	26±3	-	-	-	-	-	-	-	26±3	(2)	Nd
Ni	36±5	32±7	<41	40±5	31±7	40±3	-	-	-	-	38±3	(5)	Ni
Pb	-	-	-	38±4	37±3	40±2	-	-	30±8[b]	-	39±2	(4)	Pb
Rb	110±11	110±11	102±3	103±7	105±4	123±1	-	-	-	-	104±3	(7)	Rb
Sb	2.9±0.1	3.1±0.2	2.95±0.08	-	-	-	-	-	-	-	2.9±0.1	(3)	Sb
Sc	10.1±0.03	9.28±0.29	8.26±0.16	-	-	-	-	-	-	-	8.51±0.16	(2)	Sc
Se	1.7±0.3	-	1.5±0.4	1.4±0.4	1.4±1.2	-	-	-	-	-	1.6±0.3	(4)	Se
Si (%)	-	-	-	21.5±1.8	-	-	21.7±1.1	22.1±1.2[a]	-	-	21.8±1.1	(3)	Si
Sm	5.2±0.1	4.48±0.20	4.51±0.11	-	-	-	-	-	-	-	4.50±0.11	(2)	Sm
Sr	1040±50	-	965±59	995±60	944±37	1071±21	-	960±60[a]	-	-	1043±21	(5)	Sr
Ta	-	0.69±0.03	0.69±0.04	-	-	-	-	-	-	-	0.69±0.03	(2)	Ta
Tb	-	0.60±0.14	0.51±0.02	-	-	-	-	-	-	-	0.51±0.02	(2)	Tb
Th	9.9±0.2	9.85±0.39	8.93±0.08	-	-	-	-	-	-	-	9.89±0.20	(2)	Th
Ti (%)	-	0.23±0.10	0.22±0.05	0.22±0.02	0.24±0.02	-	0.21±0.02	0.20±0.03[a]	-	-	0.22±0.02	(6)	Ti
U	-	6.33±0.26	6.25±0.30	-	-	-	-	-	-	-	6.30±0.26	(2)	U
V	-	146±34	127±6	-	-	-	-	-	-	-	128±6	(2)	V
W	-	1.8±0.4	<2.5	-	-	-	-	-	-	-	1.8±0.4	(1)	W
Y	-	-	-	20±3	21±2	18±1	-	-	-	-	19±1	(3)	Y
Yb	-	2.06±0.07	1.98±0.04	-	-	-	-	-	-	-	2.00±0.04	(2)	Yb
Zn	130±5	-	124±3	130±10	116±4	105±4	-	-	109±11[b]	-	123±3	(5)	Zn
Zr	-	-	-	86±12	-	107±47	-	-	-	-	86±12	(3)	Zr

A = Battelle Pacific Northwest Laboratory, B = Lawrence Berkeley Laboratory, C = Lawrence Livermore Laboratory, D = University of Colorado, E = U. S. Geological Survey, a = atomic absorption spectroscopy, b = Zeeman atomic absorption spectroscopy, c = colorimetric, d = fluorimetric, e = delayed neutron, f = gamma-ray spectrometry, g = emission spectroscopy

Table 5. ELEMENTAL COMPOSITION OF FISCHER ASSAY SPENT SHALE (FASS)

	Neutron Activation Analysis			X-ray Fluorescence Spectrometry				Other			Average		
	(A)	(B)	(E)	High Energy (A)	High Energy (B)	High Energy (D)	Low Energy (B)	(A)	(B)	(D)	Conc	No. of Values	
Al (%)	-	4.05±0.13	-	-	-	-	4.0±0.2	4.04±0.25^{a}	-	4.2±0.1^{c}	4.12±0.10	(4)	Al
As	91±2	89±8	-	86±6	79±3	79±3	-	-	-	87±4^{a}	82±3	(5)	As
B	-	-	-	-	-	-	-	91±9^{g}	-	145±12^{c}	110±9	(2)	B
Ba	-	1761±55	1940±50	-	-	-	-	-	-	-	1859±50	(2)	Ba
Br	-	-	-	-	<1.8	-	-	-	-	-	<1.8	(1)	Br
Ca (%)	-	12.2±0.6	-	13.3±1.0	-	9.7±1.2	10.8±0.5	12.7±0.5^{a}	-	9.3±0.2^{a}	9.8±0.2	(5)	Ca
Cd	-	-	-	-	-	-	-	-	1.28±0.13^{b}	-	1.28±0.13	(1)	Cd
Ce	-	44±2	41±1	-	-	-	-	-	-	-	42±1	(2)	Ce
Cl	-	<1355	-	-	-	-	-	-	-	-	<1355	(1)	Cl
Co	11.0±0.2	13.1±0.4	15.8±0.2	-	<34	-	-	-	-	-	11.5±0.2	(2)	Co
Cr	34±1	43±2	52±8	-	-	-	-	-	-	-	36±1	(2)	Cr
Cs	-	5.65±0.42	5.6±0.1	-	-	-	-	-	-	-	5.60±0.11	(2)	Cs
Cu	-	-	-	68±7	66±5	47±1	-	-	-	-	67±5	(2)	Cu
Dy	-	2.28±0.12	2.7±0.1	-	-	-	-	-	-	-	2.5±0.1	(2)	Dy
Eu	0.58±0.02	0.65±0.03	0.68±0.01	-	-	-	-	-	-	-	0.68±0.01	(2)	Eu
F	-	-	-	-	-	-	-	-	-	1420±200^{a}	1420±200	(1)	F
Fe (%)	2.23±0.04	2.34±0.07	2.36±0.05	2.5±0.3	2.42±0.09	1.8±0.2	2.2±0.1	2.68±0.31^{a}	-	-	2.31±0.04	(7)	Fe
Ga	-	-	-	10.7±1.3	8.4±2.0	4.6±0.1	-	-	-	-	10.0±1.3	(2)	Ga
Ge	-	-	-	-	2.8±1.8	-	-	-	-	-	2.8±1.8	(1)	Ge
Hf	-	1.78±0.14	1.82±0.04	-	-	-	-	-	-	-	1.82±0.04	(2)	Hf
Hg	-	-	-	-	<3.9	-	-	0.041±0.001^{a}	0.035±0.003^{b}	-	0.040±0.001	(2)	Hg
In	-	<0.21	-	-	-	-	-	-	-	-	<0.21	(1)	In
Ir	-	<0.01	-	-	-	-	-	-	-	-	<0.01	(1)	Ir
K (%)	-	1.51±0.14	1.54±0.03	1.6±0.1	-	-	1.5±0.1	1.41±0.11^{a}	-	1.52±0.03^{a}	1.53±0.03	(6)	K
La	21.0±0.4	22.0±0.9	23±1	-	-	-	-	-	-	-	21.2±0.4	(2)	La
Lu	-	0.15±0.02	0.16±0.01	-	-	-	-	-	-	-	0.16±0.01	(2)	Lu
Mg (%)	-	3.0±1.3	-	-	-	-	3.1±0.2	3.2±0.1^{a}	-	2.94±0.08^{a}	3.0±0.1	(4)	Mg
Mn	-	339±11	340±10	370±30	351±32	224±25	-	375±70^{a}	-	-	342±10	(5)	Mn
Mo	-	38±5	-	39±3	-	36±2	-	-	-	28±2^{c}	37±2	(3)	Mo
Na (%)	1.62±0.03	1.74±0.05	1.76±0.04	-	-	-	1.8±0.1	1.67±0.10^{a}	-	1.90±0.07^{a}	1.77±0.04	(5)	Na
Nb	-	-	-	-	-	5.6±0.2	-	-	-	-	5.6±0.2	(1)	Nb
Nd	-	19±4	18±1	-	-	-	-	-	-	-	18±1	(2)	Nd
Ni	38±1	33±5	-	41±5	33±6	29±3	-	-	-	-	38±1	(4)	Ni
Pb	-	-	-	43±4	38±3	37±3	-	-	32±8^{b}	-	38±3	(4)	Pb
Rb	91±10	97±10	87±2	81±6	82±3	86±1	-	-	-	-	86±2	(6)	Rb
Sb	3.6±0.1	3.8±0.2	4.1±0.2	-	-	-	-	-	-	-	3.6±0.1	(2)	Sb
Sc	5.3±0.1	6.35±0.20	6.2±0.1	-	-	-	-	-	-	-	6.24±0.12	(2)	Sc
Se	5.2±0.3	-	-	4.9±0.7	4.9±1.0	-	-	-	-	4.3±0.2^{d}	5.1±0.3	(3)	Se
Si (%)	-	-	-	16.1±1.0	-	-	15.6±0.8	16.3±1.2^{a}	-	15.7±0.3^{a}	15.7±0.3	(4)	Si
Sm	3.6±0.2	3.01±0.13	3.3±0.1	-	-	-	-	-	-	-	3.4±0.1	(2)	Sm
Sr	790±50	-	860±50	810±60	770±30	771±40	-	-	-	-	790±30	(5)	Sr
Ta	-	0.47±0.02	-	-	-	-	-	-	-	-	0.47±0.02	(1)	Ta
Tb	-	0.35±0.06	0.46±0.02	-	-	-	-	-	-	-	0.45±0.02	(2)	Tb
Th	5.4±1.0	6.35±0.25	5.9±0.1	-	7.2±2.2	-	-	-	-	-	6.0±0.1	(4)	Th
Ti (%)	0.23±0.04	0.15±0.06	-	-	0.16±0.02	-	0.13±0.02	-	-	-	0.14±0.02	(3)	Ti
U	-	5.38±0.22	7±1	-	-	-	-	-	-	6.4±0.2^{e}	6.4±0.2	(2)	U
V	-	161±36	-	-	-	-	-	-	-	-	161±36	(1)	V
W	-	3.1±0.4	-	-	-	-	-	-	-	-	3.1±0.4	(1)	W
Y	-	-	-	12.6±1.9	12±2	10.2±0.7	-	-	-	-	10.6±0.6	(3)	Y
Yb	-	1.25±0.05	1.3±0.1	-	-	-	-	-	-	-	1.3±0.1	(2)	Yb
Zn	109±5	-	-	96±9	92±4	72±3	-	-	103±10^{b}	-	99±4	(4)	Zn
Zr	-	-	110±20	72±10	-	61±2	-	-	-	-	61±2	(2)	Zr

A = Battelle Pacific Northwest Laboratory, B = Lawrence Berkeley Laboratory, C = U. S. Geological Survey, D = University of Colorado, E = U. S. Geological Survey, a = atomic absorption spectroscopy, b = Zeeman atomic absorption spectroscopy, c = colorimetric, d = fluorimetric, e = delayed neutron, f = gamma-ray spectrometry, g = emission spectroscopy

RAW OIL SHALE - RAW 1B

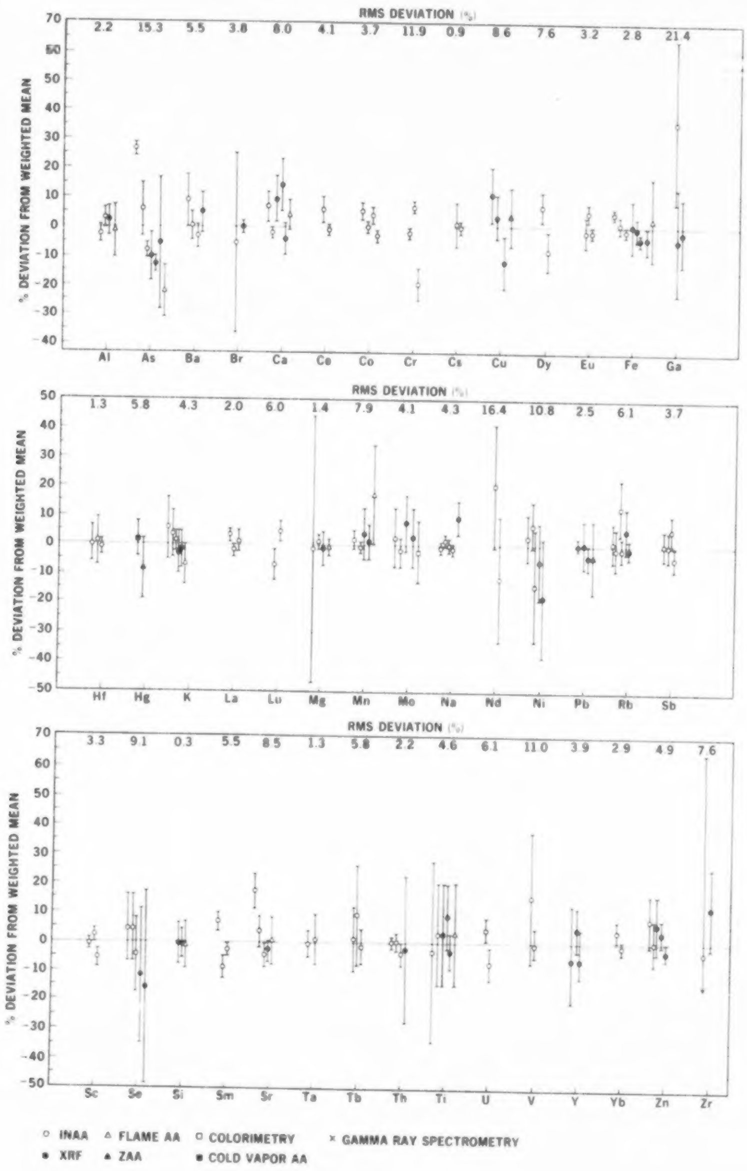

Figure 1. Relative performance of analytical techniques on raw oil shale RAW 1B

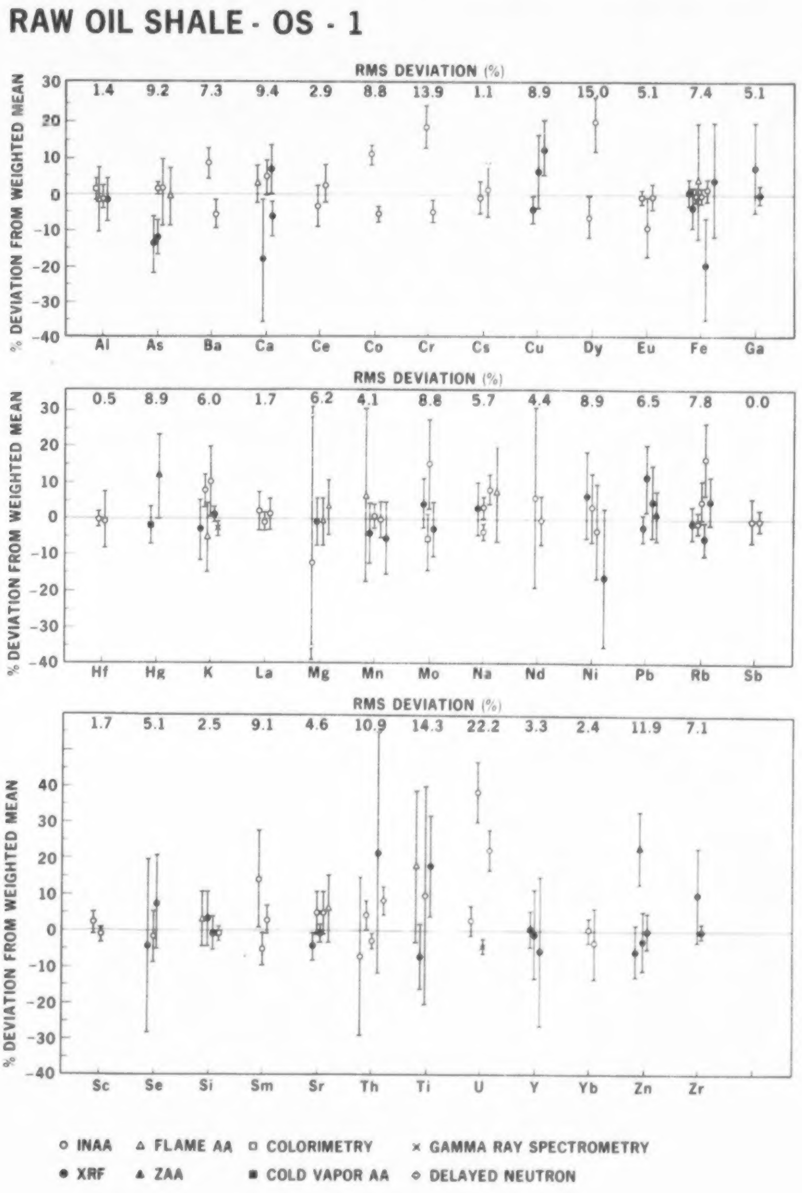

Figure 2. Relative performance of analytical techniques on raw oil shale OS-1

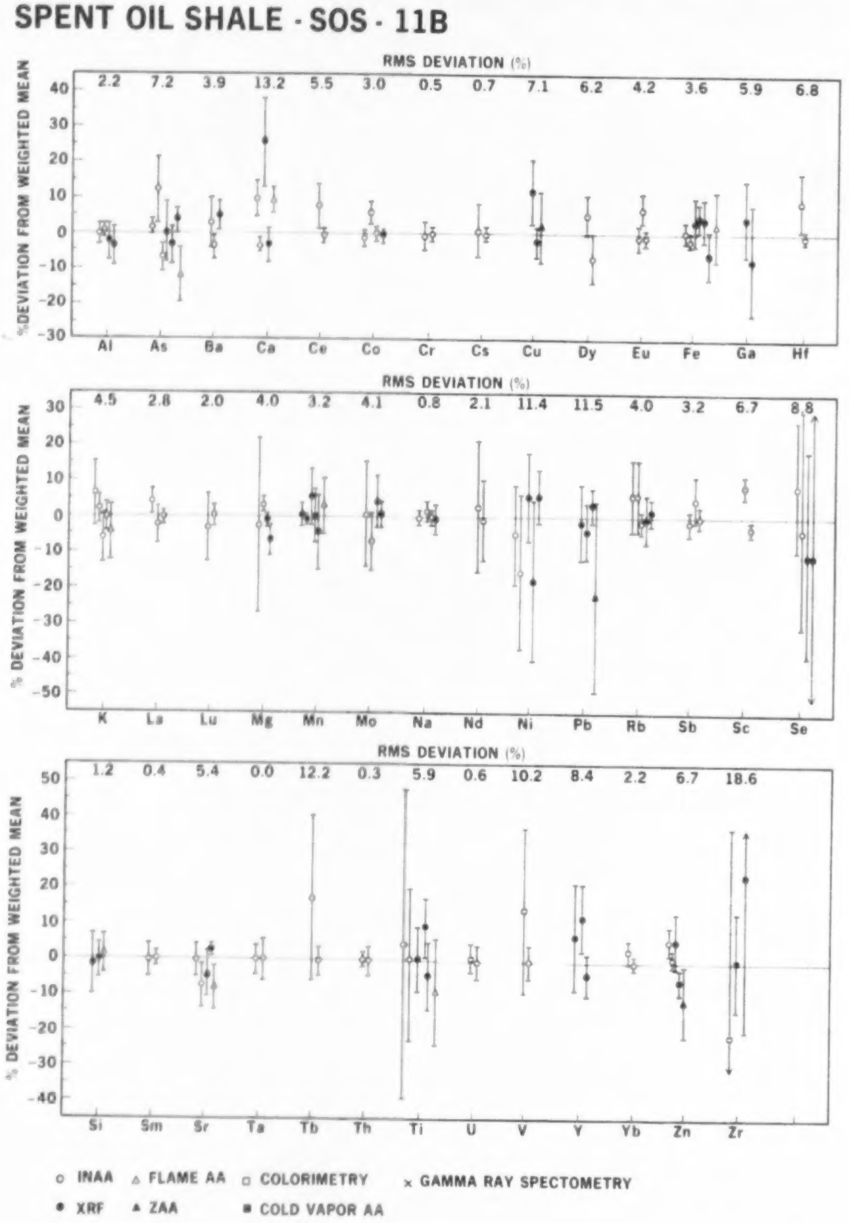

Figure 3. Relative performance of analytical techniques on spent oil shale SOS-11B

FISCHER ASSAY SPENT SHALE - FASS

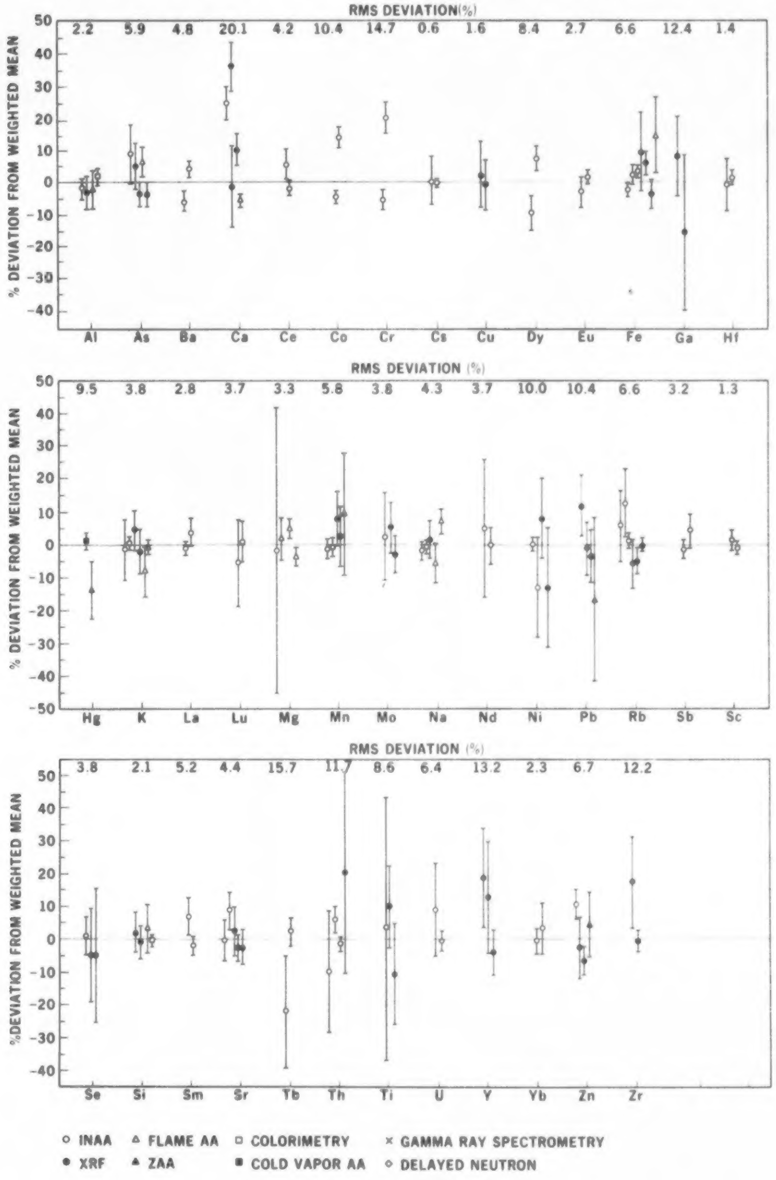

Figure 4. Relative performance of analytical techniques on Fischer assay spent shale FASS

measurements are made. Of the 52 elements surveyed, 20 were determined by more than one technique and a minimum of two measurements was obtained on 40 elements. Typically, only a single measurement, or an upper limit, was obtained for B, Cd, F, Hg, In, Ir, and Nb. Excellent agreement between laboratories and techniques was obtained for most elements on all samples. There was no significant difference in the results obtained for the raw and spent oil shale samples. The %RMS deviation was less than or equal to 10% for all elements on all samples except Ca, Cr, Ga, Pb, Ni, Tb, Zr, Y, Dy, Th, U, Zn, Ti, V, As, and Nd. The elements As, Ca, Fe, Rb, Se, Ti, and Zn were the most frequently measured elements and the major elements Al, Mg, Na, Si, and Fe were precisely measured by at least three laboratories and by using three separate techniques.

This is the first major interlaboratory comparison of energy-dispersive X-ray fluorescence spectrometry with other techniques. Intercomparison studies heretofore focused on neutron activation analysis and atomic absorption spectroscopy.[29,30] This work affords the first opportunity to assess the performance of recently developed X-ray techniques on geochemical samples for a range of elements.

More than one technique was used for the analysis of 38% of the elements (Al, As, Ca, Fe, Ga, K, Mn, Mo, Na, Ni, Pb, Rb, Se, Si, Sr, Th, Ti, U, Zn, Mg). The agreement between techniques for these elements was excellent with a few exceptions as discussed below.

Neutron activation analysis determined the most elements (38) and typically produced the most accurate and precise results. This is the only technique that was used to measure Ba, Ce, Cr, Cs, Eu, La, Sb, Sc, Sm, Yb, Dy, Cu, Nd, and Tb in all samples. Good interlaboratory agreement was obtained on all elements by INAA except Co, Cr, Dy, and Sm. Good agreement was obtained between the absolute INAA method of analysis used by LLL and the calibration method used by PNL, USGS, and LBL.

X-ray fluorescence spectrometry was used to measure 27 elements in this study. It was the only technique used for Cu, Nb, Ga, and Y. These techniques are not as precise as INAA; precisions of 10% were typical. Interlaboratory agreement was excellent and generally better than for INAA, presumably due to the larger analytical errors. Two types of XRF systems and various sample preparation and data reduction procedures were used in this study. High-energy XRF, in which the elements SI and heavier were measured, was used to analyze thin-film and thick samples using pure-element and standard rock calibration standards, respectively. Low-energy XRF, in which elements 11 through 20 were determined, was used to analyze $LiBO_2$ discs using standard rocks. These techniques agreed well with other methods of analysis except the high-energy system that used thin-film samples. That technique yielded low results for Mn and Zn and erratic results for other elements. Approximately 25% of the measurements made by the thin-specimen technique were discarded when Chauvenet's criterion was applied to the data set. This is believed to be due to X-ray absorption and matrix correction procedures.[12,13]

An analytical problem was noted for As in the raw oil shales in this study. The results obtained by INAA were typically about 15% higher than the results obtained by XRF. This same trend was evident in more than 100 samples not reported here. This disagreement was investigated by both PNL and LBL during the course of this study but its source was not identified. There are no obvious interferences in the measurement of As by either INAA or XRF. Additional work completed by some of the authors, in which material balances were calculated for various retorting processes, suggests that the problems lie with the XRF technique.

Atomic absorption spectroscopy was used to determine Hg, Al, Ca, Fe, K, Mg, Mn, Na, Sr, As, and Ti, and Zeeman atomic absorption spectroscopy was used to determine Cd, Hg, Pb, and Zn. Both of these AS techniques produced accurate and precise results. The interlaboratory and interinstrumental agreement was good except for Ca by AA in two samples and Na in one sample.

The colorimetric procedures used for Si and Mo agreed well with instrumental techniques but the fluorimetric procedure for Se yielded low results on the two samples reported here. However, good agreement between the Se fluorimetric procedure and instrumental techniques was obtained on other samples not reported here.

Additional work is required to develop reliable analytical techniques for B and F, which are important constituents in oil shales due to their leaching potential. Neither of these elements can be readily measured by the instrumental methods INAA, SRF, and AA, and chemical methods have not been adequately developed for oil shale matrices. In this study, B was measured by dc emission and colorimetrically. The results obtained by these two techniques disagree by more than 2 standard deviations of the reported errors. Similarly, F was measured by only a single technique. Additional work is required to develop and validate reliable techniques for the measurement of both B and F.

SUMMARY

Two samples each of raw oil shale and spent oil shale were prepared as reference samples and analyzed by four laboratories using neutron activation analysis, X-ray fluorescence spectrometry, atomic absorption spectroscopy, and other techniques. Excellent agreement was obtained between techniques and laboratories except for the thin-film XRF technique. The %RMS deviations were less than or equal to 10% for 85% of the values. In general, the INAA analysis procedures yielded the most accurate and precise rsults. The XRF and colorimetric methods compared well with INAA but they were not as precise. Poor interlaboratory agreement was obtained for Cr, Co, Dy, and Sm by INAA, and an analytical problem was noted for As and Zr. Additional work is required to develop and validate reliable methods for B, F, Cd, and As.

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INTERLABORATORY, MULTIMETHOD STUDY OF AN IN SITU PRODUCED OIL SHALE PROCESS WATER

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INTRODUCTION

Accurate measurement of chemical constitutents in waters from alternative fossil energy sources, such as oil shale, is essential to the orderly and timely development of those energy resources. The technology necessary to handle, contain, treat, utilize, and dispose of those waters and the information needed to predict their environmental effects and to determine regulatory compliance, require careful chemical characterization. This is particularly important for in situ oil shale technologies because about 1 barrel of water may be coproduced with each barrel of oil.[1]

Reliable chemical characterizations of synfuel process waters have been difficult to obtain. This is due to the lack of adequate standards and limitation of many available analytical methods. Concentrations of many constituents fall outside the recommended ranges for published methods, or chemical interferences produce inaccurate results. These problems have been identified by many researchers faced with making chemical measurements.[2 5] They were first nationally acknowledged when the ASTM Committee on Water, D-19, formed Subcommittee D-19.33 on "Water Associated with Synthetic Fuel Production" to address analytical problems specific to alternative fossil energy process waters.

The purpose of the present work was to obtain a careful chemical characterization of an oil shale process water designated for wide use in environmental research and to determine the suitability of existing analytical methods for this characterization. The study was carried out using an interlaboratory, multimethod approach. Samples from a larger volume, homogeneous reserve of an in situ oil shale process water were prepared and submitted to 13 laboratories for the measurement of major, minor, and trace elements and standard water quality parameters; a variety of instrumental and chemical methods was used. This paper presents the characterization of that water and discusses analytical problems specific to in situ oil shale process waters.

In Situ Oil shale Process Water

Water coproduced with shale oil and decanted from it is referred to as oil shale process water. This water originates primarily from three sources: combustion, dehydration of minerals, and groundwater[1] The ratio of water to oil ranges from 0.15 to 22, depending on the retorting atmosphere (air or inert gas) and the geographical location of the oil shale reserve.[1] This paper considers an air atmosphere process (combustion) and the oil shale reserves near Rock Springs, Wyoming.

Simulated in situ oil shale process waters produced in laboratory scale and pilot scale retorts have been characterized by several investigators.[2,7] Large variations in many measured parameters have been noted.[3 5 7] These waters are brown to yellow in color, have a pH that ranges from 8.1 to 9.4, and contain high levels of inorganic and organic constituents. The primary inorganic constitutents are HCO_3, $SO_4^{=}$, $S_2O_3^{=}$, SCN^-, F^-, Mg^{++}, Na^+, K^+, and NH_4^+.[7] The organic constitutents are primarily polar and the carboxylic acids are a major organic group.

OMEGA-9

The oil shale process water used in this work is from the 1976 Rock Springs Site 9 true in situ oil shale combustion experiment conducted by the Laramie Energy Technology Center (LETC).[8] This water has been designated "Omega-9" (Ref. 9) and that descriptor will be used in this paper. The chemical composition of this sample is specific only to itself and is not necessarily representative of in situ oil shale waters in general. Nevertheless, the analytical problems encountered in the analysis of this sample are typical of these waters due to a common matrix that includes high levels of inorganic and organic N, S, and C compounds.

Preparation

The acquisition, processing, and storage of Omega-9 are discussed in detail by Farrier et al.[9] Briefly, 12,450 gal. of process water were collected from a storage pond after 1 to 3 days residence; mixed, to ensure homogeneity, by pumped recirculation through a storage vessel; and pressure-filtered in the field through to in-line cartridge-type membrane filters with a nominal 0.4-μm exclusion. The materials in direct contact with the sample were either an inert epoxy coating, inert plastic, or stainless steel. The filter catridges were constructed of polypropylene. The upstream filter material was a compressed matrix of borosilicate microfiberglass with an acrylic resin binder, and the downstream filter was cellulose esters cast onto a cellulose web. The filter sample was partitioned into 415 polyethylene-lined, 30 gal. drums and stored at 4°C. Each laboratory participating in the study received a 500 ml sample from one of four of these drums.

Homogeneity

The homogeneity of the resulting sample with respect to some of the parameters evaluated in this study was investigated by randomly selecting three 30 gal. drums for detailed analysis. Aliquots from each drum were analyzed for representative major, minor, and trace elements and water quality parameters by two participating laboratories using techniques of known high precision. The results of those analyses are summarized in Table 1. The entries in Table 1 are average concentrations plus or minus 1 standard deviation. The number of analyses included in the average is shown in the second column. All parameters for each barrel agree to within 2 standard deviations. These data suggest that Omega-9 is homogeneous.

Stability

Stability of oil shale process waters is a significant concern. Most researchers have noted that samples stored at >4°C to 40°C develop considerable turbidity after several days. This turbidity is composed primarily of stressed rod-shaped bacterial cells.[9] These cells have a large adsorptive capacity and, within 10 days, removes significant amounts of the elements Br, Se, As, Fe, Ni and Hg from filtered samples stored at room temperature.[5]

The stability of Omega-9 water with respect to these visual changes, microbial growth, and organic content was investigated by Farrier et al.[9] and Felix et al.[10] The work of Refs. 9 and 10 indicated that storage at 4°C stabilized the water's organic content by inhibiting microbial growth. Therefore, the loss of chemical constituents due to adsorption on bacterial cells would also be significantly lessened.

An additional concern with aqueous samples is the loss of constituents by adsorption onto container walls or precipitation reactions. These effects are usually minimized by acidifying the sample to pH <2 with concentrated HNO_3.[11] [12] [13] Such acidification was not possible in this case. The sample is highly buffered by the $CO_3^=$ and NH_3 systems and contains high levels of $S_2O_3^=$. Acidification results in the precipitation of elemental S and organic acids. The precipitates act as adsorbents for some elements, interfere with most analytical measurements, and result in an inhomogeneous sample. Because the sample is well buffered, relatively large volumes of acid are required; as a result, the acid further dilutes many low level constitutents, and may contaminate the sample.

Stability of Omega-9 water for select major, minor, and trace elements was investigated by several participating laboratories. No change was noted in elemental content on storage in polyethylene-lined containers for up to 1 year at 4°C.

EXPERIMENTAL

A 500 ml aliquot of Omega-9 water, contained in an opaque plastic container, was sent to each of the 13 participating laboratories. Laboratories were selected to provide a mix of research-grade analyses, such as

Table 1. HOMOGENEITY TEST OF OMEGA-9 (mg/ℓ except as noted)[a]

Parameter	Number of Measurements	Barrel 1	Barrel 2	Barrel 3
ELEMENTAL ANALYSES[b]				
Antimony (NAA)	1	2.02 ± 0.05	2.03 ± 0.05	2.03 ± 0.05
Calcium (AAS)	1	20.3 ± 0.3	19.2 ± 0.3	16.9 ± 0.3
Copper (AAS)	1	0.09 ± 0.03	0.07 ± 0.03	0.04 ± 0.03
Iron (AAS)	1	1.70 ± 0.20	1.49 ± 0.20	1.49 ± 0.20
Lithium (AAS)	1	0.19 ± 0.01	0.18 ± 0.01	0.18 ± 0.01
Magnesium (AAS)	1	22.2 ± 0.2	21.9 ± 0.2	22.2 ± 0.2
Silicon (AAS)	1	5.2 ± 0.7	5.2 ± 0.7	5.2 ± 0.7
Silver (AAS), μg/ℓ	5	2.74 ± 0.59	3.42 ± 0.38	2.79 ± 0.35
Sodium (AAS)	1	4400 ± 100	4200 ± 100	4300 ± 100
Zinc (AAS)	1	0.30 ± 0.01	0.35 ± 0.01	0.30 ± 0.01
WATER QUALITY PARAMETERS				
Alkalinity, total (as $CaCO_3$)	1	16,900	16,900	16,000
Carbon, inorganic	3	3650 ± 365	3630 ± 365	3790 ± 380
Carbon, organic	3	1050 ± 210	1310 ± 260	1032 ± 210
Chemical oxygen demand	1	4935	5120	5105
Electrical conductivity (μmhos/cm)	1	25,200	25,600	23,500
pH	1	8.80	8.80	8.86

[a] Note: Indicated errors are one sigma for replicate analyses. If a single measurement is reported, the error is counting statistics (NAA) or signal background (AAS).

[b] NAA = neutron activation analysis; AAS = atomic absorption spectroscopy.

those performed at Department of Energy national laboratories, and routine analyses, such as are available at many commercial establishments. Most laboratories selected had prior in-depth experience analyzing a wide variety of environmental samples, including oil shale materials. The participating laboratories were coded to maintain anonymity.

Six instrumental methods were selected for detailed elemental analyses: neutron activation analysis (NAA); X-ray fluoresence spectrometry (XRF); spark source mass spectrometry (SSMS); optical emission spectroscopy (OES); plasma emission spectroscopy (PES); and atomic absorption spectroscopy (AAS). Sample preparation techniques and the suite of elements measured were left to the discretion of each laboratory. Reported results include uncertainties due to both the analysis itself and the method of sample preparation.

The measured water quality parameters include alkalinity, biochemical oxygen demand (BOD_5), $CO_3^=$, HCO_3, organic and inorganic C, conductivity, CN^-, hardness, NH_3, NH_4^+, NO_3^-, organic N, Kjeldahl N, oil and grease, pH, phenols, $PO_4^=$, solids, chemical oxygen demand (COD), and S species. The best analytical method and sample pretreatment were left to the discretion of each laboratory. In most cases, Standard Methods[11] or EPA Methods[12] were used.

The instrumental and chemical methods used to measure major, minor, and trace elements and water quality parameters in Omega-9 water are summarized in Tables 2 and 3. Additional information is available in Ref. 7.

RESULTS

The detailed analyses of major, minor, and trace elements are presented in Table 4, and of water quality parameters in Table 5. Inspection of these data indicates that there is a wide spread in values for many elements and water quality parameters. Therefore, a statistical technique[32] was used to provide a basis for discarding outlying values. The result of applying this technique to the individual values in Tables 4 and 5 is summarized in Table 6. This table presents the best value, in the judgement of the authors, for 72 elements and 28 water quality parameters.

The procedure used to analyze the data was as follows. Measurements made using a technique with known interferences were discarded. These are documented in the footnotes to Table 6. Dixon's technique was then applied to the remaining data to reject outliers.[32] This method expresses the gap between an outlier and the nearest value as a fraction of the range from the smallest to the largest value. The value of this fraction provides the basis for rejection. A range was reported when the coefficient of variations was 100%. If only upper limits were reported, the smallest upper limit was chosen except when SSMS was the analytical method. In that case, the reported upper limit was multiplied by 3 to account for a maximum factor of 3 variability noted for that technique in this study. When there were only two measurements, and when they diverged, the choice between them was based on conversations with the individual analysts. Those cases are documented in the footnotes to Table 6. Best values based on single measure-

Table 2. SUMMARY OF INSTRUMENTAL METHODS USED FOR THE ANALYSES OF OMEGA-9

Instrumental Technique	Laboratory	No. of Replicates	Sample Preparation	Special Features	Elements Detected
NAA	A	1	Evaporation at 80°C	2 irradiations and 5 decay/counting measurements	Sb, As, Ba, Cs, Cl, Co, Hf, Fe, Mo, Ni, Rb, Sc, Se, Ag, Na, Th, U, Zn
NAA	B	2	Direct analysis of liquid	2 irradiations and 5 decay/counting measurements	Al, Sb, As, Br, Cl, Sc, Se, Na
NAA	C	1	Direct analysis of liquid	2 irradiations and 3 decay/counting measurements	Sb, As, Br, Cl, Co, Cu, Mn, Mo, Na, U
NAA	D	3	Direct analysis of liquid	1 irradiation and 3 decay/counting sequences	Sb, As, Br, Cl, Co, Fe, Sc, Se, Na, Sr, U, Zn
XRF	A	3	Freeze dried	energy-dispersive system with Mo x-ray tube; counted for 20 min	As, Br, Ca, Cu, Fe, Mn, Ni, Rb, Se, Sr, Ti, U, V, Zn, Zr
XRF	B	3	Air dried	energy-dispersive system with Ag secondary source; counted for 100 min	As, Br, Ca, Cu, Mo, Rb, Se, Zn, Zr
XRF	N	1	Direct analysis of liquid	wavelength-dispersive system with Pt x-ray tube; counted for 100 sec	Cl
SSMS	E	2	Carbon slurry dried with infra-red lamp	m/e fractions analyzed by ion-sensitive photoplates and the disappearing line technique	Al, Sb, As, Ba, Br, Cd, Cs, Cr, Co, Cu, Ga, Ge, Hf, I , Fe, La, Pb, Mn, Mo, Ni, Nb, P, Pr, Rb, Se, Si, Ag, Sr, Ta, Te, Sn, Ti, W, U, V, Y, Zn, Zr
PES	D	3	Direct analysis of liquid	System used Ar plasma jet and Echelle grating spectrometer	As, Ba, B, Ca, Cu, Mg, Mo, P, Si, V, Zn
OES	F	1	Evaporation, ignition at 450°C and grinding	D.C. arc source coupled to grating spectrographs	Sb, Ba, B, Cr, Co, Fe, Pb, Li, Mn, Mo, Rb, Sr, Ti, V, Zr
AAS	A	3	Direct analysis on liquid except Hg which was evaporated at 80°C	Zeeman AAS; graphite rod atomization	As, Se, Cd, Ag, Hg
AAS	C	2	Digestion; Ref. 14	flame atomization; corrections for matrix effects	Ca, Mg, Na, K, Fe, Si, As, Se, Sb
AAS	D	3	Ref. 15	flame atomization; correction for Na matrix	Na, Mg, Si, Fe, Li, Ca, Cu, Zn
AAS	E	2	Ref. 12, 16	flame atomization except K, Na by flame emission	Ca, K, Mg, Na, Hg
AAS	F	1	Ref. 12	flame atomization	Na, K, As, Se, Hg, Zn, Ca, Mg, Al
AAS	G	1	Ref. 12, 17	flame atomization	Na, K, Ca, Mg, Se, Pb, Cd
AAS	H	3-10	Ref. 15, 18	flame atomization	Mn, Ni, Zn, K, Fe, Ca, Sn
AAS	I	2	Ref. 19	flame atomization; correction for Na matrix	Ca, Mg

Table 3. SUMMARY OF CHEMICAL METHODS USED FOR THE ANALYSIS OF OMEGA-9

Chemical Parameter	Laboratory	Method	Interferences	Reference
Alkalinity	A, F, J, N	Titrimetric	Soaps, oils	11, 12
Arsenic	N	Ag diethyldithiocarbonate	Co, Hg, Ni, Ag, Cu, Cr, Mo, Sb	11
BOD_5	F	5 day incubation	Various toxicants	12
Boron	C	Dianthrimide method	Unknown	–
	I	–	Unknown	14
	E	–	Unknown	11
Calcium	J	EDTA titrimetric	$PO_4^{=}$, Ba, Sr, alkalinity	11
Carbon (HCO_3^-, $CO_3^{=}$)	C, F, H, I, K	Computed from alkalinity	NH_3, B, Si, organic bases	11, 12
Carbon, inorganic	A, C	–	Unknown	11
	H	–	Unknown	20
Carbon, organic	K, C	Sealed ampoule	Unknown	–
	H, M, N	Direct	Volatile organics	11
	A	Indirect	Unknown	11
COD	A, F, J, I	Chemical oxidation	$S_2O_3^{=}$, $S_4O_6^{=}$	11,12
	N	Chemical oxidation	$S_2O_3^{=}$, $S_4O_6^{=}$	21, 22
Chloride	F, H, J	$Hg(NO_3)_2$ titration	Organics, I^-, Br^-	11, 12
	E	–	–	23
	C, I	Technicon Autoanalyzer	Br^-, I^-, SCN^-	12
Conductivity	A, G, I	Instrumental	Soaps, oil, grease	11, 12
Cyanide	F	Colorimetric	Color	12
	C, N	Distillation/specific ion electrode	Fatty acids	11
Fluoride	D, E, F, G, N	Specific ion electrode	Unknown	11, 12
	C	Technicon Autoanalyzer/ specific ion electrode (C) or Technicon Autoanalyzer (N)	Unknown	–
	I	SPADNS	Unknown	12
Hardness	H	EDTA titration	Unknown	11
	I	Computed	–	–
Magnesium	J	Computed	See Ca, hardness	11
Nitrogen, ammonia	A, H, J	Distillation/titrimetric	Amines	11
	C	Distillation/idophenol	Unknown	12
	J, N	Specific ion electrode	Amines	12, 24
Nitrogen, Kjeldahl	C	Technicon Autoanalyzer	Unknown	–
	F, H, I	Distillation	Amines plus others excluded	11, 12, 25
Nitrogen, organic	J	Distillation/titrimetric	Amines plus others excluded	11
	H	Computed	Amines plus others excluded	–
Nitrogen, nitrate	F	Colorimetrically	SCN^-	12
Oil and grease	C	Freon extraction	Organics	12
pH	A, C, F, G, H, I, J, N	Electrometrically	Soaps, oils, grease	11, 12
Phenols	A, C, F, J, N	Colorimetrically	Para-substituted phenols	11, 12
Phosphorus, orthophosphate	J	Stannous chloride	SiO_2, As, F^- $S_2O_3^{=}$, SCN^-	11
	F	Colorimetrically	Unknown	12
Phosphorus, total	C, F	Technicon Autoanalyzer	Unknown	12
Potassium	I	Technicon Autoanalyzer	Unknown	–
Silicon	I	–	Unknown	14
Sodium	I	Technicon Autoanalyzer	None known	–
	J	Specific ion electrode	Unknown	–
Solids	A, F, G, H, I, J, N	Gravimetric	NH_3, NH_4^+, HCO_3^-, $CO_3^{=}$	11, 12
Sulfur, sulfate	A, C, F, J	Turbidimetric	None known	11, 12
	G, N	Gravimetric	None known	12
	I	Chloranilate	None known	12
Sulfur, sulfide	A, N	Titrimetric	S compounds, volatile organics	12, 26
	C	Qualitative	None known	11
Sulfur, sulfite	F	Titrimetric	Organics	12
Sulfur, thiocyanate	A, C	Colorimetric	None known	11
Sulfur, tetrathionate	C	Colorimetric	Unknown	27, 28
Sulfur, thiosulfate	C	–	Unknown	27, 28
	J	Titrimetric	Unknown	–
Sulfur, total	C	Digestion	Unknown	29
	E, H	Gravimetric	None known	30
Uranium	G	–	None known	31

ments are enclosed in parentheses; these values are uncertain and require additional analysis for validation.

The use of this procedure with the elemental data (Table 4) resulted in the rejection of seven measurements as outliers and of six others due to chemical interferences. For the water quality parameters (Table 5), one measurement was rejected as an outlier and ten were rejected due to chemical interferences. Ranges were reported for six elements and three water quality parameters.

Elemental Characterization

The best values in Table 6 indicate that of the 72 elements measured in Omega-9 water (1) 32 were detected by two or more laboratories or techniques and fair agreement was obtained; (2) a range was reported for six elements; (3) 22 were below the detection limit of all techniques used; and (4) only a single measurement was used for an additional 12 elements.

The coefficient of variation reported in the last column of Table 6 demonstrates the agreement obtained among different laboratories and techniques. The average coefficient of variation for the 32 elements measured was 30%. Of those 32, the coefficient of variation was ≦ 10% for 3 elements (Cl, Cr, Na); 10% - < 20% for 7 elements (Br, F, Mo, K, U, Zn, K); 20% - < 30% for 7 elements (Sb, As, B, Hf, Fe, Rb, Sc); and ≧ 30% for 15 elements (Ba, Cd, Ca, Co, Cu, Mg, Mn, Ni, P, Se, Si, Ag, Sr, S, Zr).

Although the 30% average coefficient of variation obtained in this study is large compared with that obatined in some intercomparison studies using other sample types,[34] the results are encouraging. The present sample is highly contaminated, chemically complex, and the concentration of many measured constituents is close to the detection limit of applied techniques. The average concentration for 29 elements measured by two or more techniques is 6.3 mg/l. Additionally, other intercomparisons have focused on a single instrumental method.[34] This study employed six separate analytical techniques for which a wide range of sample preparation methods was used. Thus, the sources of variability include not only instrumental error and sample handling, but uncertainties due to different sample preparation methods.

A range was reported for Al, Li, Pb, Hg, Sn, and Ti. The large variations for these elements are probably due to interferences or to sample handling and preparation methods. Since all of these elements are environmentally important, work should be directed at discovering the source of the variability and correcting it.

Water Quality Parameters

The best values in Table 6 indicate that of the 28 water quality parameters measured in Omega-9 water, 16 were detected by two or more laboratories and fair agreement obtained; a range was reported for 3; 1 was below the detection limit; and 8 were measured by only a single laboratory.

Table 4. ELEMENTAL ANALYSIS OF OMEGA-9 (mg/ℓ)

	Instrumental Methods[a]											
Element	X-ray Fluorescence Spectrometry		Instrumental Neutron Activation Analysis				Spark Source Mass Spectrometry	Emission Spectroscopy		Atomic Absorption Spectroscopy	Chemical and other Methods[a]	Element
								Optical	DC Plasma			
	A	D	B	C	D	A	E	F	D			
Aluminum	–	–	19.1±4.1	–	–	<420	0.30±0.06	–	<0.03	<1[F], 1[H]	–	Aluminum
Antimony	–	–	1.81±0.36	1.81	2.03±0.03	1.66±0.16	2.6±0.7	1.0±0.1	–	2.5[C]	–	Antimony
Arsenic	0.92±0.02	1.09±0.02	0.84±0.18	0.88	1.17±0.03	1.3±0.3	0.58±0.08	–	1.0±0.2	1.0±0.1[A], 1.1[C], 1.3[F]	0.7[N]	Arsenic
Barium	0.63±0.17[b]	–	< 4.4	–	–	0.41±0.24	1.1±0.0	1.0±0.1	0.39±0.04	<10[H]	–	Barium
Beryllium	–	–	–	–	–	–	<0.002	<0.01	–	–	–	Beryllium
Bismuth	–	–	–	–	–	–	<0.004	<0.01	–	–	–	Bismuth
Boron	–	–	–	–	–	–	–	40±4	23±1	30[H]	22[C],22±0[E], 26[I]	Boron
Bromine	2.70±0.08	2.44±0.1	2.07±0.42	3.0	2.65±0.09	–	1.8±0.0	–	–	–	–	Bromine
Cadmium	–	–	< 3.3	–	–	<0.8	0.001±0.000	–	<0.01	0.0022±0.0001[A], <0.1[G]	–	Cadmium
Calcium	12.4±0.6	7.5±1.4	<410	–	–	<2200	–	–	7.3±0.4	c	16.3[J]	Calcium
Cerium	–	–	< 0.23	–	–	<0.026	–	–	–	–	–	Cerium
Cesium	–	–	< 0.045	–	–	0.0021±0.0003	0.004±0.001	<0.01	–	–	–	Cesium
Chlorine	–	–	793±160	895	870±40	741±35	–	–	–	–	d	Chlorine
Chromium	<0.10	–	< 0.24	–	<0.06	<0.02	0.019±0.000	0.02±0.002	–	–	–	Chromium
Cobalt	<0.27	–	< 0.091	0.028	0.020±0.003	0.022±0.001	0.028±0.000	0.05±0.01	–	<0.1[G]	–	Cobalt
Copper	0.13±0.10	0.17±0.07	<90	0.075	–	<5	0.09±0.04	<0.01	0.04±0.03	0.07±0.03[D],0.1[G]	–	Copper
Dysprosium	–	–	< 0.18	–	–	<0.04	<0.002	–	–	–	–	Dysprosium
Europium	–	–	< 0.049	–	–	<0.0013	<0.002	–	–	–	–	Europium
Fluorine	–	–	<3300	–	–	–	–	–	–	–	e	Fluorine
Gallium	<0.021	–	<17	–	–	<8.2	0.004±0.000	<0.01	–	–	–	Gallium
Germanium	<0.021	–	<260	–	–	–	0.013±0.004	<0.01	–	–	–	Germanium
Gold	–	–	< 0.0048	–	–	<0.0068	<0.009	–	–	–	–	Gold
Hafnium	–	–	< 0.074	–	–	0.0123±0.0010	0.017±0.001	–	–	–	–	Hafnium
Holmium	–	–	< 0.063	–	–	–	–	–	–	–	–	Holmium
Indium	–	–	< 0.1	–	–	<0.02	–	<0.01	–	–	–	Indium
Iodine	–	–	< 8.1	–	–	–	0.59±0.30	–	–	–	–	Iodine
Iridium	–	–	< 0.00037	–	–	<0.00006	<0.013	–	–	–	–	Iridium
Iron	1.01±0.28	–	<23	–	0.60±0.2	1.1±0.7	1.1±0.3	1.5±0.2	–	1.1[C],1.45±0.19[D], 1.2[G],1.5[H]	–	Iron
Lanthanium	–	–	< 0.3	–	–	<0.17	0.006±0.001	<0.01	–	–	–	Lanthanium
Lead	<0.075	–	<18000	–	–	–	0.0045±0.0007	0.02	–	<0.2[G]	–	Lead
Lithium	–	–	–	–	–	–	–	0.8±0.1	–	0.18±0.01[D]	–	Lithium
Lutetium	–	–	< 0.0059	–	–	<0.006	<0.002	–	–	–	–	Lutetium
Magnesium	–	–	<550	–	–	–	–	–	19.9±1.6	f	28.6[J]	Magnesium
Manganese	0.05±0.03	–	< 0.86	0.058	–	<0.23	0.12±0.04	0.12±0.01	<0.25	<0.1[G]	–	Manganese
Mercury	<0.045	–	< 0.14	–	–	<0.13	–	–	–	g	–	Mercury
Molybdenum	–	0.61±0.03	< 3.5	0.58	–	0.68±0.15	2.3±0.8	0.50±0.05	0.63±0.03	–	–	Molybdenum
Neodymium	–	–	< 0.29	–	–	<0.08	<0.003	–	–	–	–	Neodymium
Nickel	0.05±0.03	–	< 7	–	–	0.06±0.02	0.03±0.01	<0.01	<0.01	<0.1[G], 0.08[H]	–	Nickel
Niobium	–	–	<130	–	–	–	0.002±0.000	–	–	–	–	Niobium
Osmium	–	–	< 0.017	–	–	–	<0.02	–	–	–	–	Osmium
Palladium	–	–	< 9.2	–	–	–	<0.017	–	–	–	–	Palladium
Phosphorus	–	–	<2300	–	–	–	6.7±0.6	–	2.81±0.26	–	3.0[C], 0.28[F]	Phosphorus
Platinum	–	–	< 0.49	–	–	–	<0.025	–	–	–	–	Platinum
Potassium	–	–	<1500	–	–	<700	–	–	–	h	56[I]	Potassium
Praseodymium	–	–	<170	–	–	–	0.0020±0.0014	–	–	–	–	Praseodymium
Rhenium	–	–	< 0.024	–	–	–	–	–	–	–	–	Rhenium
Rhodium	–	–	< 3.7	–	–	–	<0.005	–	–	–	–	Rhodium
Rubidium	0.21±0.02	0.11±0.02	< 1.4	–	–	0.16±0.02	0.17±0.00	0.04±0.04	–	–	–	Rubidium
Ruthenium	–	–	< 0.52	–	–	–	<0.014	–	–	–	–	Ruthenium
Samarium	–	–	< 0.12	–	–	<0.0013	<0.004	–	–	–	–	Samarium

Table 4. CONTINUED

Element	Instrumental Methods[a]											Element
	X-ray Fluorescence Spectrometry		Instrumental Neutron Activation Analysis				Spark Source Mass Spectrometry	Emission Spectroscopy		Atomic Absorption Spectroscopy	Chemical and other Methods[a]	
								Optical	DC Plasma			
	A	D	B	C	D	A	E	F	D			
Scandium	–	–	0.00145±0.00036	–	0.0011±2%	0.0010±0.0003	<0.01	<0.01	–	–	–	Scandium
Selenium	0.18±0.01	0.18±0.03	0.38±0.08	–	0.17±0.04	0.25±0.03	0.094±0.000	–	–	i	–	Selenium
Silicon	–	–	<3900	–	–	–	18±4	–	9.2±0.4	9.8^{C},5.1±0.7^{D},4.0^{F}	2.0^{I}	Silicon
Silver	–	–	< 0.28	–	–	0.0044±0.0014	0.0025±0.0001	<0.01	–	0.0029±0.0006^{A} <0.1^{G}	–	Silver
Sodium	–	–	4210±840	4550	4503±24	4530±130	–	–	–	j	4500^{I},3685±212^{J}	Sodium
Strontium	1.12±0.05	–	<24	–	1.03±0.07	<16	1.6±0.1	0.72±0.07	–	–	–	Strontium
Sulfur	–	–	<27000	–	–	–	–	–	–	–	2340^{C},989±14^{E}, 2700^{H}	Sulfur
Tantalum	–	–	< 0.013	–	–	<0.0003	0.045±0.025	–	–	–	–	Tantalum
Tellurium	–	–	< 1.5	–	–	–	0.001	–	–	–	–	Tellurium
Terbium	–	–	< 0.0065	–	–	<0.0009	–	–	–	–	–	Terbium
Thallium	–	–	<450	–	–	–	<0.002	<0.01	–	–	–	Thallium
Thorium	<0.063	–	< 0.024	–	–	0.0037±0.0003	<0.006	–	–	–	–	Thorium
Thulium	–	–	<0.013	–	–	–	–	–	–	–	–	Thulium
Tin	–	–	< 5.3	–	–	–	0.001	<0.01	–	10^{H}	–	Tin
Titanium	0.14±0.10	–	<71	–	–	<43	1.3±0.0	0.03±0.003	<0.02	2^{H}	–	Titanium
Tungsten	–	–	<0.62	–	–	<0.15	0.010±0.000	–	–	–	–	Tungsten
Uranium	0.59±0.03	–	< 0.91	0.51	0.52±0.07	0.41±0.02	1.08±0.18	–	–	–	0.65^{G}	Uranium
Vanadium	0.11±0.08	–	< 0.89	–	–	<5	0.068±0.000	0.04±0.004	0.13±0.01	–	–	Vanadium
Ytterbium	–	–	< 0.025	–	–	<0.002	<0.005	<0.01	–	–	–	Ytterbium
Yttrium	<0.05	–	<2800	–	–	–	0.001±0.000	<0.01	–	–	–	Yttrium
Zinc	0.33±0.04	0.30±0.11	< 3	–	0.33±0.01	0.26±0.06	0.7±0.4	–	0.34±0.02	k	–	Zinc
Zirconium	0.49±0.27	0.88±0.03	<2000	–	–	–	1.0±0.0	0.51±0.05	–	–	–	Zirconium

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[a] Superscript letters A through N are coded descriptors for the laboratories making measurements.

[b] Ba measurement made on a different x-ray system by measuring the Ba Kα x-rays induced in the sample prepared by laboratory A for NAA analysis with the 60 KeV gamma ray of ^{241}Am.

[c] 8.0^{C}, 17±2^{D}, 6.45±0.07^{E}, 19^{F}, 14^{G}, 10.8^{H}, 12^{I}, 12.1^{N}

[d] 3900^{C}, 2530±127^{E}, 950^{F}, 1685±505^{H}, 4100±285^{I}, 3677±55^{J}, 822^{N}

[e] 56^{C}, 53^{D}, 68±0^{E}, 77^{F}, 60^{G}, 56^{I}, 50^{N}

[f] 12^{C}, 22.2±0.3^{D}, 26.5±0.7^{E}, 20^{G}, 10.4^{H}, 19^{I}, 19.3^{N}

[g] 0.021±0.003^{A}, <0.0002^{E}, <0.02^{F}, 0.0003^{G}, 0.0016^{N}

[h] 43^{C}, 51±0^{E}, 37^{F}, 56^{G}, 34^{H}, 53^{N}

[i] 0.07^{C}, 0.12^{F}, 0.25^{G}, 0.4^{H}

[j] 4290±114^{B}, 4100^{C}, 4402±32^{E}, 4400^{F}, 4400^{G}, 613^{H}, 4430^{N}

[k] 0.33±0.03^{D}, 0.24^{F}, 0.3^{G}, 0.37^{H}

Table 5. ANALYSIS OF OMEGA-9 FOR WATER QUALITY PARAMETERS (mg/ℓ)

Parameter	Laboratory[a]								
	(A)	(C)	(F)	(G)	(H)	(I)	(J)	(N)	Other
Alkalinity	16,600 ± 520	–	15,600	–	–	–	16,100 ± 344	16,600	–
Biochemical Oxygen Demand, 5-day	–	–	740	–	–	–	–	–	–
Carbon, Bicarbonate (as HCO_3^-)	–	15,100	15,300	–	13,255 ± 920	16,000	–	–	–
, Carbonate (as $CO_3^=$)	–	2100	660	–	3020 ± 780	0	–	–	–
, Inorganic (as C)	3690 ± 86	3400	–	–	2917 ± 231	–	–	–	–
, Organic (as C)	1130 ± 160	920	–	–	780	–	–	1300	1035 ± 104^K, 851 ± 18^M
Chemical Oxygen Demand	5052 ± 83	–	7700	–	–	18,000	5679 ± 481	4154	–
Conductivity (μmhos/cm)	24,800 ± 1100	–	–	18,200	–	18,100 ± 850	–	–	–
Cyanide (as CN^-)	–	0.90	0.42	–	–	–	–	2.9	–
Hardness, Total (as $CaCO_3$)	–	–	–	–	62 ± 6	110	–	–	–
Nitrogen, Ammonia (as NH_3)	4070 ± 90	–	–	–	3218 ± 0	–	3846 ± 95	3643	4198 ± 680^J
, Ammonium (as NH_4^+)	3290 ± 75	4890	–	–	2321	3400 ± 140	3300 ± 80	–	3600 ± 585^J
, Kjeldahl (as N)	–	4000	3400	–	3280 ± 164	3000	–	–	–
, Nitrate (as NO_3^-)	–	–	0.17	–	–	–	–	–	–
, Organic (as N)	–	–	–	–	630	–	148 ± 28	–	–
Oil and Grease	–	580	–	–	–	–	–	–	–
pH	8.82 ± 0.03	8.5	8.6	8.5	9.0 ± 0.1	8.2	8.7	8.9	–
Phenols	56 ± 2	59	110	–	–	–	29.4	45	–
Phosphorus, Orthophosphate (as $PO_4^{\equiv}$)	–	6.7	0.08	–	–	–	24.6	–	–
Solids, Fixed	13,721 ± 10	–	–	–	–	–	13,135 ± 50	–	–
Solids, Total	–	–	–	14,200	14,340 ± 40	–	14,100 ± 494	–	–
Solids, Total Dissolved	–	–	13,900	14,200	14,340 ± 40	14,400	–	14,200	–
Sulfur, Sulfate (as $SO_4^=$)	2020 ± 160	2040	1200	1890	2500	1900	1710 ± 80	1875	–
, Sulfide (as S)	116 ± 12	0.0	–	–	–	–	–	176	–
, Sulfite (as S)	–	–	925	–	–	–	–	–	–
, Tetrathionate (as $S_4O_6^=$)	–	280	–	–	–	–	–	–	–
, Thiocyanate (as SCN^-)	110 ± 2	136	–	–	–	–	–	–	–
, Thiosulfate (as $S_2O_3^=$)	–	2225	–	–	–	–	3260	–	–

[a] Letters A–N are coded descriptors for laboratories making the measurements.

Table 6. CHARACTERIZATION OF OMEGA-9 TRUE IN-SITU SHALE PROCESS WATER (mg/ℓ)

	Total[a]	Included in Best Value				
Element	Number of Measurements	Number[a] of Measurements	Number of Labs	Number of Techniques	Best Value[b] (mg/ℓ)	Coefficient of Variation
ELEMENTAL ANALYSES						
Aluminum	6	6	6	6	<0.03 - 19.1	
Antimony	7	7	6	4	1.9 ± 0.5	28%
Arsenic	12	12	7	6	1.0 ± 0.2	22%
Barium	7	5	4	3	0.71 ± 0.33	47%
Beryllium	2	1	1	1	<0.006	
Bismuth	2	1	1	1	<0.01	
Boron	6	6	6	4	27 ± 7	26%
Bromine	6	6	4	3	2.4 ± .4	18%
Cadmium	6	2	2	2	0.0016 ± 0.0008	53%
Calcium	14	12	10	4	12 ± 4	35%
Cerium	2	1	1	1	<0.026	
Cesium	4	1	1	1	(0.0021 ± 0.0003)[c]	
Chlorine	11	5	5	2	824 ± 61[d]	7.4%
Chromium	6	2	2	2	0.02 ± 4%	3.6%
Cobalt	8	5	5	3	0.030 ± 0.012	40%
Copper	10	7	4	3	0.10 ± 0.04	44%
Dysprosium	3	1	1	1	<0.006	
Europium	3	1	1	1	<0.0013	
Fluorine	8	7	7	3	60 ± 9	16%
Gallium	5	1	1	1	(0.004 ± 0.000)	
Germanium	4	1	1	1	(0.013 ± 0.004)	
Gold	3	1	1	1	<0.005	
Hafnium	3	2	2	2	0.015 ± 0.003	23%
Holmium	1	1	1	1	<0.063	
Indium	3	1	1	1	<0.01	
Iodine	2	1	1	1	(0.59 ± 0.30)	
Iridium	3	1	1	1	<0.00006	
Iron	10	9	6	5	1.2 ± 0.3	25%
Lanthanum	4	1	1	1	(0.006 ± 0.001)	
Lead	5	2	2	2	0.0045 - 0.02	
Lithium	2	2	2	2	0.18 - 0.8	
Lutecium	3	1	1	1	<0.006	
Magnesium	10	9	8	3	20 ± 6	30%
Manganese	8	4	4	4	0.09 ± 0.04	44%
Mercury	8	4	4	1	0.0003 - 0.021	
Molybedenum	7	5	5	4	0.60 ± 0.07	11%
Neodymium	3	1	1	1	<0.009	
Nickel	8	4	3	4	0.06 ± 0.02	38%
Niobium	2	1	1	1	(0.002 ± 0.000)	
Osmium	2	1	1	1	<0.06	
Palladium	2	1	1	1	<0.05	
Phosphorus	5	4	4	3	3.2 ± 2.6	83%
Platinum	2	1	1	1	<0.08	
Potassium	9	7	7	2	47 ± 9	19%
Praseodymium	2	1	1	1	(0.0020 ± 0.0014)	
Rhenium	1	1	1	1	<0.024	
Rhodium	2	1	1	1	<0.015	
Rubidium	6	4	2	3	0.16 ± 0.04	25%
Ruthenium	2	1	1	1	<0.042	
Samarium	3	1	1	1	<0.0013	
Scandium	5	3	3	1	0.0012 ± 0.0002	20%
Selenium	10	10	8	3	0.21 ± 0.11	53%
Silicon	7	6	5	4	8 ± 6	72%
Silver	6	3	2	3	0.003 ± 0.001	31%
Sodium	13	12	11	3	4333 ± 244	5.6%
Strontium	6	4	4	4	1.12 ± 0.36	33%
Sulfur	4	3	3	2	2010 ± 900	45%
Tantalum	3	1	1	1	(0.045 ± 0.025)	
Tellurium	2	1	1	1	(0.001)	
Terbium	2	1	1	1	<0.0009	
Thallium	3	1	1	1	<0.006	
Thulium	1	1	1	1	<0.013	
Thorium	4	1	1	1	(0.0037 ± 0.0003)	
Tin	4	4	4	4	0.001 - 10	
Titanium	7	7	6	6	<0.02-2	

Table 6. CONTINUED

	Total[a]	Included in Best Value				
Element	Number of Measurements	Number[a] of Measurements	Number of Labs	Number of Techniques	Best Value[b] (mg/ℓ)	Coefficient of Variation
Tungsten	3	1	1	1	(0.010 ± 0.000)	
Uranium	7	5	4	3	0.55 ± 0.07	13%
Vanadium	6	2	2	2	0.12 ± 0.01	12%
Ytterbium	4	1	1	1	<0.002	
Yttrium	4	1	1	1	(0.001 ± 0.000)	
Zinc	11	9	5	5	0.31 ± 0.04	13%
Zirconium	5	4	3	4	0.73 ± 0.25	35%
WATER QUALITY PARAMETERS						
Alkalinity (as $CaCO_3$)	4	4	4	1	16,200 ± 480	3.0%
Biochemical Oxygen Demand, 5-day	1	1	1	1	(740)	
Carbon, Bicarbonate (as HCO_3^-)	4	0	0	0	(15,940)[e]	
Carbon, Carbonate (as $CO_3^=$)	4	0	0	0	(500)[e]	
Carbon, Inorganic (as C)	3	3	3	2	3340 ± 390	12%
Carbon, Organic (as C)	6	6	4	3	1003 ± 192	
Chemical Oxygen Demand	5	4	4	1	8100 ± 5700	70%
Conductivity (μmhos/cm)	3	3	3	1	20,400 ± 3840	19%
Cyanide (as CN^-)	2	2	2	2	0.42 - 2.9	
Hardness, Total (as $CaCO_3$)	2	1	1	1	(110)[f]	
Nitrogen, Ammonia[g] (as NH_3)	5	5	5	3	3795 ± 390	10%
Nitrogen, Ammonium (as NH_4^+)	6	6	5	3	3470 ± 830	24%
Nitrogen, Kjeldahl (as N)	4	4	4	2	3420 ± 420	12%
Nitrogen, Nitrate (as NO_3^-)	1	1	1	1	(0.17)	
Nitrogen, Organic (as N)	2	2	2	2	148 - 630	
Oil and Grease	1	1	1	1	(580)	
pH	8	8	8	1	8.65 ± 0.26	3.0%
Phenols	5	5	5	1	60 ± 30	51%
Phosphorus, Orthophosphate (as $PO_4^=$)	3	3	3	3	0.08 - 24.6	
Solids, Fixed	2	2	2	1	13,430 ± 415	3.1%
Solids, Total	3	3	3	1	14,210 ± 120	0.85%
Solids, Total Dissolved	5	5	5	1	14,210 ± 193	1.4%
Sulfur, Sulfate (as $SO_4^=$)	8	7	5	3	1990 ± 250	13%
Sulfur, Sulfide (as S)	3	1	1	1	(0.0)[h]	
Sulfur, Sulfite (as S)	1	0	0	0	<20[i]	
Sulfur, Tetrathionate (as $S_4O_6^=$)	1	1	1	1	(280)	
Sulfur, Thiosulfate (as $S_2O_3^=$)	2	2	2	2	2740 ± 730	27%
Sulfur, Thiocyanate (as SCN^-)	2	2	2	1	123 ± 18	15%

[a] The first column is the total number of measurements including upper and lower limits. The second column is the number of measurements used to compute the best value.

[b] The following rules were used to determine best values: (1) The smallest upper limit is reported unless that upper limit is for SSMS. In that case, the SSMS upper limit is multiplied by 3. (2) A range is reported if the coefficient of variation is greater than 100%. (3) Best values based on a single measurement are enclosed in parentheses. (4) Best values based on 2 or more measurements are determined using Dixon's procedure (32) following exclusion of values resulting from analytical errors. The reported error is 1 standard deviation if the number of measurements is greater than 1. Otherwise, it is the error reported by the laboratory making the measurements.

[c] The NAA value was selected based on conversations with the individual analysts.

[d] The measurements made using the Technicon Autoanalyzer and the mercuric nitrate methods were excluded due to interferences.

[e] Calculated using methodology shown in Table 8 and for C_T = 3336 mg/ℓ, pH = 8.6.

[f] Total hardness is the sum of polyvalent cations reported as $CaCO_3$. The reported value is consistent with value computed from Ca and Mg analyses reported in Table 6.

[g] This is the sum of NH_3 and NH_4^+.

[h] The presence of a very low sulfide level was verified by laboratories A and C using the qualitative AgS precipitation test.[39]

[i] The method used to measure sulfite has strong interferences. Based on qualitative analyses made by laboratory C, the sulfite level is <20 mg/ℓ. (Ref. 39).

Quantitative data based on two or more measurements were obtained for alkalinity, organic and inorganic C, conductivity, NH_3, NH_4^+, Kjeldahl N, pH, phenols, solids, $SO_4^=$, $S_2O_3^=$, SCN^-, and COD. The coefficient of variation reported in the last column of Table 6 demonstrates the agreement obtained among different laboratories and techniques. The average coefficient of variation for the 16 parameters is 18%, significantly better than the 30% coefficient obtained for the elemental analyses. However, in general, the accuracy obtained for the water quality parameters is poorer than that for the elements. (This will be discussed in the section on "Analytical Considerations." Of these 16 parameters, the coefficient of variation was $< 5\%$ for 5 parameters (alkalinity, pH, solids); $5\% - < 20\%$ for 7 parameters (inorganic and organic C, conductivity, HN_3, Kjeldahl N, $SO_4^=$, SCN^-); and $\geq 20\%$ for 4 parameters (COD, NH_4^+, phenols, $S_2O_3^=$). However, the average concentration of 13 water quality parameters measured by two or more laboratories (pH, phenols, SCN^- excluded) is 8,200 mg/l, which is 1,300 times higher than that of the average concentration for 29 elements (6.3 mg/l).

The results obtained for CN^-, organic N, and $PO_4^\equiv$ varied widely and only a range is reported in Table 6. Coefficients of variation greater than 50% were obtained for phenols and COD. The variability in these parameters is probably due to significant interferences and/or stability problems.

Relative Instrumental Performance

An approximate criterion of performance for each laboratory and instrumental technique is summarized in Table 7. Table 7 presents the mean, standard deviation, coefficient of variation, and uncertainty in the coefficient of variation for normalized measurements. Normalized measurements were computed by dividing each value in Tables 4 and 5 by the best value from Table 6. Only elements or waters quality parameters detected by two or more laboratories or techniques for which a coefficient of variation is reported in Table 7 are included in the normalized measurements. The coefficient of variation is a measure of accuracy for the elemental analyses; the normalized mean, if significantly different from 1, indicates systematic errors of measurement. Performance increases as the normalized mean approaches 1 and as the coefficient of variation decreases.

Because of the uncertainties in the true value of the abundances of an element when determined by averaging the results of different laboratories, there is an uncertainty in the coefficient of variation. This uncertainty is reported in the last column of Table 7. Therefore, small differences may not be significant. Of the 11 laboratories/techniques used for elemental analyses, 8 have coefficients of variation between 15% and 30% and three have a coefficient of variation between 50% and 70%. There is no statistically significant difference in the performance within each of these groups, but there is between the groups. Thus, the performance of XRF, NAA, PES, and AAS in this study was significantly better than that of SSMS, OES, and other methods. Similarly, of the eight laboratories reporting water quality analyses, five have coefficients of variation between 15% and 25% and two have coefficients of variation between 35% and 40%. The coefficient of variation for the eighth laboratory, G, falls into a group of 1. Thus, there was a statistically significant difference in performance for analysis of water quality parameters.

The NAA, XRF, and AAS results are the most consistent and accurate of the instrumental techniques evaluated. OES, PES, and SSMS have normalized means significantly different from 1, suggesting systematic errors. However, SSMS detected more elements than any other technique evaluated and consistently had the lowest detection limit. The "other" techniques shown in Table 7 include specific ion electrode and colorimetric and wet chemical measurements. The deviant mean and high coefficients of variation for these measurements are due primarily to chemical interferences encountered with the chlorine measurements.

ANALYTICAL CONSIDERATIONS

Many of the analytical techniques investigated in this study are inadequate for the analysis of complex matrices such as oil shale process waters. Standard analytical methods including Standard Methods,[11] EPA's methods,[12] ASTM methods,[25] and USGS methods[14] are often not applicable to these types of waters due to the interferences and to the extremely high or low levels of many parameters. Each method should be evaluated on a case-by-case basis when used for highly complex samples. Nevertheless, most participating laboratories used these methods without modification. This points to the urgent need to develop and publish methods specific to complex sample types not heretofore widely analyzed.

Although many of the wet chemical techniques evaluated gave reproducible results, the accuracy of measurement was poor due to interferences. This is true for Cl^-, $S^=$, $SO_3^=$, solids, and $CO_3^=$.

The primary interferences for wet chemical measurements are high concentrations of organic or inorganic S, C, and N compounds; the presence of strong color and emulsified oil and grease; and the diversity of organic compounds. Some C, N, and S compounds combine with analytical reagents, producing erroneous results. This type of interference affects the measurement of COD, $S^=$, $SO_3^=$, and Cl^-. The presence of color and oil and grease interfere with some colorimetric and electrode measurements. This type of interference may affect both the precision and accuracy of measurement of F^-, conductivity, pH, alkalinity, $CO_3^=$, HCO_3^-, PO_4^-, phenols, and Cl^-.

The precision obtained for many of the water quality parameters using the same method in different laboratories was poor and generally outside of quoted precisions.[11] [12] This is true of COD, phenol, inorganic and organic C, conductivity, NH_3, $SO_4^=$, $S^=$, and $SO_3^=$. The poor precision is probably due to differneces in pretreatment selected by the individual laboratories to mitigate suspect interferences, and to the presence of color, oil, and grease, all of which interfere with colorimetric and electrode methods.

The determination of HCO_3^-, $CO_3^=$, NH_3, NH_4^+, $S^=$, H_2S, and other species may depend on equilibrium calcuations. The ionic strengths of Omega-9 and of similar waters, however, is so high ($I \geq 0.5$) that the usual assumption

Table 7. LABORATORY AND TECHNIQUE PERFORMANCE EXPRESSED AS A NORMALIZED AVERAGE AND COEFFICIENT OF VARIATION

Elemental Analyses[a]	**Number of Elements Included in Normalized Average (N)**	**Normalized Average ($\bar{X} \pm 1\sigma$)**	**Coefficient of Variation $\left[\frac{1\sigma}{\bar{X}}\right]100$**	**Uncertainty in Coefficient of Variation $\frac{\left[\frac{1\sigma}{\bar{X}}\right]100}{\sqrt{2(N-1)}}$**
X-ray Fluorescence (A)	14	0.96 ± 0.21	22%	4%
X-ray Fluorescence (D)	9	1.02 ± 0.31	30%	8%
Neutron Activation Analysis (A)	16	0.97 ± 0.22	23%	4%
Neutron Activation Analysis (B)	7	1.09 ± 0.35	32%	9%
Neutron Activation Analysis (C)	10	0.94 ± 0.17	18%	4%
Neutron Activation Analysis (D)	12	0.94 ± 0.20	21%	5%
Spark Source Mass Spectrometry (E)	23	1.29 ± 0.78	60%	9%
Optical Emission (F)	12	1.14 ± 0.60	53%	11%
D.C. Plasma Emission (D)	11	0.88 ± 0.25	28%	6%
Atomic Absorption Spectroscopy	13	1.03 ± 0.17	17%	3%
Other	12	1.15 ± 0.80	70%	15%
Water Quality Parameters[a]				
Laboratory A	12	1.00 ± 0.15	15%	3%
Laboratory C	9	1.05 ± 0.17	16%	4%
Laboratory F	7	1.05 ± 0.39	37%	11%
Laboratory G	5	0.96 ± 0.05	5.2%	2%
Laboratory H	10	0.90 ± 0.20	22%	5%
Laboratory I	8	1.11 ± 0.44	40%	11%
Laboratory J	10	0.92 ± 0.19	21%	5%
Laboratory N	8	0.94 ± 0.23	24%	6%

[a] Letters A - N are coded descriptors for laboratories making measurements.

of infinite dilution is not valid. Approximations, such as the Debye-Huckel or Davies, to correct equilibrium constants for ionic strength are invalid for $I > 0.5$ (Ref. 35). Laboratory measurements of appropriate equilibrium constants need to be made so these species can be accurately determined.

Fewer interferences were identified for the instrumental methods (NAA, XRF, SSMS, AAS, OES, PES) than for the chemical methods of analysis. The extremely high Na level in the sample limited the sensitivity of NAA measurements where radiochemical separation was not used and interfered with some AAS, OES, and PES measurements. However, the overall precision of measurements was poorer than for the chemical methods. A major reason for this is that the mean concentration of elements determined instrumentally was 6.3 mg/l; it was 8,200 mg/l for the water quality parameters. Another factor is the variety of sample preparation methods used. There are few standard methods for instrumental analysis, except AAS.

A number of the more significant interference problems noted in this study are summarized and discussed below; other interferences are summarized in Table 3. The discussion is limited to those constituents that occur at high levels in Omega-9 or to those with interferences that are understood by the authors. Additionally, routine chemical methods that appear to be suitable for analysis of waters like Omega-9 are identified.

Chlorine

A significant analytical problem attends the measurement of Cl in oil shale process water. The four methods used to measure Cl--NAA, XRF, $Hg(NO_3)_2$ titration, and the Technicon AutoAnalyzer--produced highly variable results. Although NAA and XRF measure total Cl and the chemical methods measure Cl^-, this distinction cannot account for the large variablility apparent in Table 4.

The Cl data have a trimodal distribution. The results obtained by NAA and the single XRF measurement average 824 ± 61 mg/l; by the Technicon AutoAnalyzer, 4,000 ± 140mg/l; and by the $Hg(NO_3)_2$ titration method, 2,211 ± 1,171 mg/l. The NAA and Technicon AutoAnalyzer results are consistent within each method while the $Hg(NO_3)_2$ results show large dispersion.

The Technicon AutoAnalyzer and the $Hg(NO_3)_2$ method both have interference problems that were not considered in running the tests; those problems are discussed below. Therefore, these results have not been used to compute the best value for Cl in Table 6. In contrast, there is no known interference for Cl measured by NAA or XRF methods used in this work. Consequently, the NAA and XRF measurements were used to compute the Cl value shown in Table 6.

The high values and dispersion obtained with the chemical methods can be explained by examining the analytical methods in more detail. The $Hg(NO_3)_2$ method is recommended in Standard Methods[11] and by the EPA[12] for the analysis of Cl^- in waters. It consists of titrating an acidified sample with $Hg(NO_3)_2$ using diphenylcarbazone as the endpoint indicator. Tests with this method in one of the author's laboratories indicate that there is an interference problem.

The method is based on the reaction:

$$2Cl^- + Hg^{++} \rightleftarrows HgCl_2\ (aq) \qquad (1)$$

However, in the presence of other constituents that react with Hg, the method gives results that are high.

A number of constituents present in Omega-9 may form precipitates with the Hg used for titration. These include SCN^-, $SO_4^=$, $S_2O_3^=$, and some carboxylic acids. During titration, a gelatinous precipitate forms before the endpoint is reached. Its formation has two effects: first, the endpoint is postponed, which causes a high result; and second, the muddy precipitate makes detection of the endpoint difficult. This latter point probably accounts for the dispersion in the $Hg(NO_3)_2$ titration results. An additional minor interference is the simultaneous titration of Br^- and I^-.

Oxidation with $KMnO_4$ removes the interference for some waters, yielding results equivalent to those obtained by instrumental analysis. In the $KMnO_4$ method developed at the laboratory of one author, the sample is diluted 1:10 with distilled water, acidified to $pH < 1$ with HNO_3, heated to boiling, cooled in a water bath, 5 ml 0.2 N $KMnO_4$ added, and the sample titrated with 0.141 N $Hg(NO_3)_2$ when Hg reacts with Cl^- to form $HgCl_2$. In the presence of ferric ion, SCN^- forms the highly colored ferric thiocyanate in proportion to the original Cl^- concentration. The presence of SCN^- and color interfere with this method. Additionally, Hg reacts with constituents other than Cl^-, analogous to the $Hg(NO_3)_2$ titration interference, yielding high results.

Sulfide

Sulfide is measured quantitatively by the methylene blue or iodine titrimetric methods[11] [12] [26] and qualitatively by the lead acetate paper, antimony, or silver foil tests.[11] In this work, the qualitative methods and the iodine titrimetric methods following a CO_2 purge into $An(C_2H_3O_2)_2$ or $CdSO_4$ were used. Table 5 indicates that there is considerable disagreement between these two methods. The titrimetric method yielded an average $S^=$ concentration of 146 mg/l-S and the qualitative test indicated that $S^=$ was absent.

The presence of reducing agents in oil shale process waters interferes with the quantitative tests. Notable among these are $S_2O_3^=$ and various organics. The high (2,743 mg/l) $S_2O_3^=$ concentration in Omega-9 would prevent the formation of the blue color in the methylene blue method. If the sample is titrated directly, $S_2O_3^=$, phenol, and unsaturated fatty acids will react with I^- during titration, again yielding high results.

Both Standard Methods[11] and EPA methods[12] recommend pretreatment to eliminate these interferences. Pretreatment consists of precipitating the

$S^=$ as ZnS by adding 2 N $Zn(C_2H_3O_2)_2$ followed by separation of the precipitate. This pretreatment was not used in this study as the presence of high levels of reducing agents was not suspected. Therefore, results reported using the titrimetric method are in error and are not used to compute the best value for $S^=$ summarized in Table 6.

The qualitative tests, on the other hand, are relatively free of interferences. Results obtained by laboratory C and subsequently by the authors suggest that $S^=$, if present, occurs at low levels in Omega-9.

It is recommended that pretreatment be used if standard analytical methods are used for the measurement of $S^=$ in oil shale process waters. The $Zn(C_2H_3O_2)_2$ pretreatment procedure should be evaluated in the laboratory to determine if it is suitable for oil shale retort waters.

Organic Carbon

The data in Table 5 suggest that there is an analytical problem associated with the measurement of TOC in Omega-9. The reported TOC values range from 780 to 1,300 mg/l and average 1,003 ± 193 mg/l. These values were obtained using several commercially available instruments and both direct methods (inorganic C removed by acidifying and purging) and indirect methods (computed from independent measurements of total and inorganic C).

There are three principal sources of error in the standard TOC procedure when it is applied to oil shale process waters. These are: (1) the presence of suspended or emulsified organics and large organic particles that are not taken up in microsyringes; (2) the formation of precipitates when the sample is acidified; and (3) the loss of volatiles on purging with N_2 or on storage. The loss of volatiles and precipitate formation are eliminated when the indirect method is used.

Heterogeneities due to suspended materials, large organic particles, or precipitates may be minimized by using large sample size for analysis. If that is not possible, an effort to homogenize the sample should be made. Laboratory M noted that precipitation formation was alleviated by using dilute 1M HCl instead of concentrated HCl for acidification.

Volatile organic carbon was measured at 250 mg/l by laboratory M. Those volatiles could be lost during N_2 purging or during storage since the samples were not maintained under an N_2 blanket. A method to eliminate the loss of volatiles during the purging has been published[33] and should be investigated for application to oil shale process waters.

Chemical Oxygen Demand

The chemical oxygen demand (COD) of a water is a measure of the oxygen equivalent of the organic matter that is oxidized by a strong chemical oxidant. The parameter is conventionally used to assess the performance of biological treatment processes and to estimate the effect of waste discharges on the oxygen level in receiving waters; in addition, it is sometimes used to regulate the discharge of organic wastes. The COD is measured in terms of the amount of potassium dichromate ($K_2Cr_2O_7$) reduced by a sample during a 2-hour reflux in a solution of boiling, 50% H_2SO_4 and in the presence of a Ag_2SO_4 catalyst. $HgSO_4$ catalyst. $HgSO_4$ is added to complex Cl^- and thus prevent its oxidation to Cl_2. Essentially complete (theoretical) oxidation of many organic compounds is obtained in the presence of the catalyst. Straight-chain aliphatic compounds, aromatic compounds, and many N compounds are incompletely oxidized.[11] [36]

The COD data summarized in Table 5 range from 4,154 to 18,000 mg/l, a range that is significantly outside of the precision of the method reported in Standard Methods.[11] The fact that in-laboratory precision is good while between-laboratory precision is poor suggests that the method is very sensitive to some part of the procedure that is not carefully controlled since all laboratories but one used the same method. The variability may be related to the fact that neither Standard Methods[11] nor the EPA methods[12] specify an upper limit for the COD concentration. The ASTM COD method,[36] which is procedurally identical to these two methods, specifies an upper limit of 800 mg/l COD for a 50-ml sample treated with 25 ml of 0.25 N $K_2Cr_2O_7$. The maximum COD that can be measured using a 50 ml sample and 25 ml of 0.25 N $K_2Cr_2O_7$ is 1,000 mg/l (Ref. 37). A sample with a COD greater than 1,000 mg/l, such as Omega-9, would therefore have to be diluted to bring it within the range for the method. Thus, different dilutions could cause the noted variability. The high Cl^- concentration could also contribute to the variability if the Hg added to complex Cl^- were complexed by constituents other than Cl^-. Both the Standard Methods and EPA method for COD should be modified to include appropriate statements on the upper limits of the method.

Any inorganic compound that is oxidized by $K_2Cr_2O_7$ in an acid medium will contribute to the measured COD and give a high value. The principal known interferences from this source in Omega-9 are $S_2O_3^-$ and $S_4O_6^-$ (Refs. 38, 39). For example, the $S_2O_3^-$ is readily oxidized by $K_2Cr_2O_7$ to SO_4^- in acid media as follows:

$$4\ Cr_2O_7^{=} + 3\ S_2O_3^{=} + 26\ H^+ \rightarrow 6\ SO_4^- + 8\ Cr^{+3} + 13\ H_2O \qquad (2)$$

Thus, for each milligram of $S_2O_3^=$ present in a sample, 0.285 ml of 0.25 N $K_2Cr_2O_7$ will be consumed, yielding a high result. The effect of this on the measured COD can be theoretically computed using Eq. (2). Since Omega-9 has an $S_2O_3^-$ concentration of 2740 mg/l, the theoretical COD due to oxidation of $S_2O_3^-$ to SO_4^- is 1270 mg/l COD.

The standard COD test[11] [12] should be modified to correct for the oxidation of inorganic S compounds before the test is applied to oil shale process waters containing high levels of compounds. Experimental work is required to develop a method to eliminate this interference. Additionally, the ability of the recommended quantities of Ag_2SO_4 and $HgSO_4$ to, respectively, catalyze the oxidation of certain organics and complex Dl^-, should be verified experimentally for oil shale process waters.

Solids

Total dissolved and fixed solids were measured with good precision; however, the significance of those measurements for waters similar to Omega-9 is questionable.

Total dissolved solids (TDS) as operationally defined in Standard Methods[11] and by EPA[12] is the residue remaining after a sample has been filtered and dried at 103°-105°C or at 180°C. This parameter is intended to be a good indicator of total dissolved salts, which are not significantly lost on heating. However, this parameter is a poor indicator of the dissolved salts in waters similar to Omega-9. This could be a significant problem if this parameter is used to make regulatory decisions or to design treatment facilities.

The degree by which the measured TDS differs from the total dissolved salts present in Omega-9 is indicated by the following. The average measured TDS for this water is 14,210 mg/l while the calculated total dissolved salts is 30,300 mg/l. The factor of 2 difference between the measured and calculated TDS is typical of the results obtained with these waters.

The species $CO_3^=$, HCO_3^-, NH_3, and NH_4^+ constitute over 65 weight percent of the dissolved salts present in Omega-9. On heating at 103°-105°C, these species are lost from solution through the formation of volatile salts or by stripping out dissolved gases. Linstedt, Daniel, and Bennett[33] investigated lyophilization and evaporation of Omega-9 at room temperature, as an alternative to evaporation at 103-105°C or 180°C, and found that neither procedure gave satisfactory results. Substantial losses of NH_4HCO_3 occurred even at freezing temperatures. Therefore, the TDS determination, irrespective of the drying temperatures, gives a value that is significantly low for oil shale process waters and is not representative of the dissolved salts present.

The same considerations apply to total solids. Work needs to be directed at developing a method to measure both total solids and TDS in these types of waters that accurately reflects the level of salts present. This may be approached by determining a temperature at which a significant fraction of the ammonia and carbonate species is lost without loss of other components. The TDS could then be measured by running the standard analysis at this elevated temperature and adjusting the value obtained by adding to it NH_4^+, $CO_3^=$, and HCO_3. Alternatively, the CO_2 and NH_3 lost during the TDS test could be collected and determined gravimetrically.

Alkalinity, Biocarbonate, Carbonate

Conventionally,[11 12] HCO_3^- and $CO_3^=$ are determined from alkalinity and pH measurements. However, that method is not valid for oil shale process waters due to the presence of buffering components other than the $CO_3^=$ system (ammonia, borate, silicate, organic bases) and the high ionic strength of the water. The presence of these species results in an overestimation of $CO_3^=$ when the Standard Method[11 12] is used.

Since all of the participating laboratories used conventional methods to determine HCO_3 and CO_3^- the measurements reported in Tables 4 and 5 were not used to determine the best values shown in Table 6. Instead, an alternative method was used to compute those species. This method is described below and is recommended for the measurement of HCO_3^- and CO_3^- in any water not buffered exclusively by the CO_3^- system.

An alternative way to determine HCO_3 and $CO_3^=$ is to measure the total inorganic C and pH and to use equilibrium expressions to compute the distribution of HCO_3 and CO_3^-. This method is discussed by Stumm and Morgan[35] and is summarized and applied to Omega-9 water in Table 8. Note that the equilibrium constants K_1 and K_2 must be adjusted for the ionic strength of the sample. Alternatively, a back titration may be used in conjunction with the usual strong acid titration.

The computed value for HCO_3^- compares favorably with the average of all analytical determinations in Table 4 (15,940 vs 14,800 mg/l). However, the CO_3^- values are not in agreement (500 vs 1,720 mg/l). This is primarily due to the variation in measured pH and the presence of buffering components which are neutralized during titration above the $CO_3^=$ equivalence point. This is confirmed for Omega-9 by equivalence points at 7.5 and 4.3.

Recommended Analytical Methods

Based on the results of this study and the authors' experience with analytical instrumentation, the following instrumental techniques are recommended for the analysis of waters similar to Omega-9.

Instrumental Methods -

XRF: As, Br, Ca, Cu, Fe, Ni, Rb, Se, Sr, Ti, U, V, Zn, Zr, Mo, Cl

NAA: Sb, As, Br, Cl, Co, Mn, Hf, Ce, Ba, Fe, Mo, Ni, Sm, Se, Na, Sr, U, Zn

AAS: Se, Ca, Fe, Na, Zn, Mg, K

Chemical and Other Methods -

The following chemical methods are recommended for analysis of oil shale process waters pending further laboratory evaluation.

1. Arsenic: silver diethyldithiocarbamate[11]
2. Chloride: $KMnO_4$ oxidation/$Hg(NO_3)_2$ titration (this work)
3. Sodium: Technicon AutoAnalyzer
4. Uranium: Fluorimetric[31]
5. Fluoride: Specific ion electrode[11]
6. Sulfate: Gravimetric[11]
7. Thiocyanate: Colorimetric[11]
8. Total Sulfur: Gravimetric[30]

Table 8. COMPUTATION OF HCO_3^- AND $CO_3^=$ FROM MEASUREMENTS OF INORGANIC C AND pH

Carbonate species distribution

$$[HCO_3^-] = \alpha_1 C_T$$

$$[CO_3^=] = \alpha_2 C_T$$

$$\alpha_1 = \left[\frac{[H^+]}{K_1} + \frac{K_2}{[H^+]} + 1\right]^{-1}$$

$$\alpha_2 = \left[\frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]}{K_2} + 1\right]^{-1}$$

C_T = dissolved inorganic carbon, mg/ℓ as C

Ionic strength

$$I = 1/2 \sum_i C_i Z_i^2$$

Z_i = ionic charge

C_i = molar concentration

Adjustment of equilibrium constants

$$pK' = pK - AZ^2\left[\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right]$$

$A \simeq 0.5$

Application to Omega-9

$I = 0.5$

$pK_1 = 6.22$ at 25°C

$pK_2 = 9.80$ at 25°C

$\alpha_1 = 0.94$

$\alpha_2 = 0.06$

$C_T = 3340$ mg/ℓ

$HCO_3^- = 15{,}940$ mg/ℓ as HCO_3^-

$CO_3^= = 500$ mg/ℓ as $CO_3^=$

pH = 8.65

9. Inorganic Carbon: Carbon Analyzer[11]
10. Alkalinity: Titrimetric[11 12]
11. $HCO_3^-/CO_3^=$: Calculation from inorganic C and pH (Table 8)

These recommendations are based on collaborative results from several methods or from extensive knowledge of the technique. Emission techniques and SSMS are not recommended because the data base compiled in this study is not adequate to assess their general performance. Additionally, the performance of these techniques as measured by the normalized average and coefficient of variation (Table 7) was poor.

Elements other than those listed above may be determined by XRF, NAA, and AAS. The specific elements measured depend on the design of the instrumentation. A good example of this is XRF. Laboratories using XRF in this study used energy-dispersive systems and high energy X-rays (except laboratory N). Alternatively, a wavelength-dispersive system using low-energy X-rays could be exployed and another set of elements, including Na, Ca, Fe, Si, Mg, and Cl, determined.

Based on the work presented here, the 11 chemical methods appear adequate for use with waters like Omega-9. However, the authors encourage additional collaborative work on these methods to establish their validity on a range of oil shale process waters before any major analytical work is undertaken. The other chemical methods used in this study require modification to correct for interferences.

CHEMICAL SIGNIFICANCE OF OMEGA-9 WATER

The composition of this water is influenced by the intrusion of groundwater into the formation (see Ref. 3 for groundwater composition), process operating conditions, and oil shale composition. The water-to-oil ratio of 22 obtained during the acquisition of the Omega-9 sample[1] suggests that approximately 22 parts of groundwater were mixed with 1 part of combustion water plus dehydration water. The chemistry of this specific water is dominated by an alkaline pH and the presence of high levels of organic and inorganic C, N, and S as well as Na and Cl. The high level of organic and inorganic C, N, and S is typical of oil shale process waters and the high level of Na and Cl are atypical of these waters and probably originated from groundwater intrusion.

The TDS, as determined from the sum of the individual ions, is about 30,300 mg/l, which is roughly equal to the TDS of seawater. The principal ions, present at levels greater than 1,000 mg/l, are Na^+, NH_4^+, HCO_3^-, $S_2O_3^=$, and $SO_4^=$; they constitute about 95% of the total salts present on a weight basis. Other constituents present at levels of 10 to 1,000 mg/l are B, Ca, Mg, K, $CO_3^=$, Cl^-, F^-, $S_4O_6^=$, and SCN^-. Constituents present at levels of from 1 to 10 mg/l are Sb, As, Br, Fe, P, Si, and Sr. Other constituents are present at levels below 1 mg/l.

A charge balance for Omega-9 water is presented in Table 9. This balance is based on the best values summarized in Table 6. The percent

Table 9. CHARGE BALANCE FOR OMEGA-9 WATER

CATIONS

	mg/ℓ	meq/ℓ
Calcium	12	0.60
Magnesium	20	1.65
Potassium	46	1.18
Sodium	4333	188.47
Ammonium	3470	192.71
TOTAL		384.61

ANIONS

	mg/ℓ	meq/ℓ
Bicarbonate	15,940	261.27
Carbonate	500	16.66
Chloride	824	23.24
Fluoride	60	3.16
Sulfate	1990	41.44
Thiosulfate	2740	48.93
Tetrathionate	280	2.50
Thiocyanate	123	2.12
		399.32

$$\% \text{ Variation} = \left[\frac{|x_1 - x_2|}{x_1 + x_2}\right] 100 = 1.9\%$$

variation (1.9%) is considerably less than the recommended limit of 3%. The good agreement of the charge balance lends credibility to the accuracy of some of the analytical results determined in this study.

SUMMARY

This study has evaluated existing chemical and instrumental methods for the characterization of an oil shale process water. It demonstrated that many standard analytical methods cannot be used to accurately measure water quality parameters in these complex waters. Methods specific to these waters need to be developed and published. The following methods were found to give incorrect results when used on waters like Omega-9: (1) $Hg(NO_3)_2$ titration and Technicon AutoAnalyzer methods for Cl^-; (2) titrimetric methods without pretreatment for $S^=$; (3) gravimetric method for solids; and (4) the permanganate oxidation method for COD. Other methods, including those for CN^-, phenols, PO_4, and $CO_3^=$, do not yield reproducible results. There may be interferences in other methods used in this study but there are presently inadequate data to assess them. Some existing chemical methods for the measurement of alkalinity, $SO_4^=$, inorganic C, Na, SCN^-, As, and total S, and the methods presented in this work for $CO_3^=$, HCO_3^-, and Cl^- may be adequate for routine analyses following limited additional laboratory testing.

The instrumental methods used were found to be free of interferences, with the exception of the high Na concentration. Since this is not typical of oil shale process waters, this may not be a problem for other oil shale process waters. However, instrumental methods are subject to variations due to differences in sample preparation and the fact that most of these techniques produce precision data for a subset of the total set of elements reported. Results obtained with SSMS and the emission techniques were poor compared with those obtained with other instrumental methods. SSMS consistently gave the lowest detection limit but had the poorest precision of all instrumental methods evaluated. XRF, NAA, and AAS produced precise and accurate results.

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ROLE OF ORGANIC COMPOUNDS IN THE MOBILITY OF TRACE METALS

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ABSTRACT

Preliminary studies of the possible mobilization of trace metals in retorted shale by organic compounds have involved a class fractionation of crude shale oil followed by gas chromatographic and trace metal analysis of the fractions. A reasonably good column chromatographic separation was achieved with neutral alumina packing by successive elutions with solvents of increasing polarity. The results from the trace metal analyses experiments indicated a tendency toward association of the metal ion with specific fractions from the separation, in particular the nitrogenous bases.

INTRODUCTION

The scale of shale oil recovery operations anticipated for the State of Colorado has raised many questions regarding the environmental impact on water quality, since large quantities of retorted shale and retort wastewater will be produced by the various operations of shale oil recovery.[1]

Of special importance are the nitrogen- and sulfur-containing compounds which may promote the mobilization of toxic trace elements in retorted shale (such as cadmium, molybdenum, arsenic and selenium) through complexation or chelation. Such metallo-organic complexes are sometimes more toxic than the simple inorganic species and frequently exhibit a "solubilization" effect.[2] This effect would increase the mobility of the trace element and introduce it in an altered form in the biosphere, thereby becoming available for uptake by plants and animals.

The present study has focused on the development of a method for the separation of the bulk organics from the nitrogen- and sulfur-containing compounds found in shale oil. Trace metal analyses by atomic absorption spectrophotometry of the various fractions obtained from this separation have been conducted to determine whether selected metal ions tend to be associated with specific classes of compounds.

CONCLUSIONS

Studies on the fractionation of shale oil have shown that a fairly good class separation is achieved by absorbtion of the crude oil onto neutral alumina followed by successive elutions with solvents of increasing polarity. The results of trace metal analyses for lead, zinc, arsenic, cadmium, and selenium, on the column fractions, suggest specific metal association with classes of organic compounds, notably the nitrogenous bases.

Mutagenicity studies performed at Oak Ridge National Laboratory on shale oil samples have found the highest mutagenic activity to be exhibited by the nitrogen-containing fractions.

In view of the toxicity of three metals (cadmium, arsenic and selenium) found to be associated with the nitrogen-containing fractions of the shale oil and the mutagenic activity also associated with these fractions, the study of the speciation of metallo-organic complexes is of great importance and much more work is required to fully assess the potential danger of groundwater contamination.

RECOMMENDATIONS

The study of the speciation of metal ions and the identification of metallo-organic complexes in water samples from shale oil recovery operations will provide information essential for minimizing adverse effects on the quality of groundwater in the area. The results of this study indicate that there is a tendency of metal ions to associate with specific chemical classes of compounds in the crude oil. It is now necessary to determine whether these associations are present in the water samples and to identify any metallo-organic complexes. In addition, more information is needed related to leaching and transport processes in the retorted shale. Studies in these areas have been initiated with the recent acquisition of several water samples.

MATERIALS AND METHODS

SAMPLE INVESTIGATED

This study was conducted on samples of Paraho shale oil.* These samples have been stored longer than desirable and the data obtained should be interpreted bearing in mind the age of the samples.

This oil sample is not to be considered representative of the Paraho process. It was used in these preliminary studies to develop methods which will be used in the analysis of water samples.

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*(Collected by Dr. Thomas Wildeman; Day 2; Period 0000-0800; Sample 50-10; Split #2; N_2 - F; 8/17/77.)

ANALYTICAL METHODS

Gas Chromatographic Analysis

The detection of individual components of each fraction was accomplished by gas chromatography employing a flame ionization detector (FID) and a nitrogen-phosphorous detector (NPD). The gas chromatographic columns used in this study were high resolution glass capillary columns. The columns were ∿20 m long and coated dynamically with 10% OV-101 in methylene chloride. FID analyses were conducted on a Hewlett-Packard HP5830A, while an HP5730A was used for the NPD analyses. Both instruments are equipped with Hewlett-Packard capillary inlet systems. The operating conditions for the HP5830A equipped with an FID were: column temperature held at 70°C for 4 minutes, then increased 4°/min to 230° for 16 minutes; nitrogen carrier gas ∿1 ml/min at 7 psig inlet pressure; hydrogen, 30 psig; air, 30 psig; injection port temperature, 250°C; detector temperature 300°C. Analyses with nitrogen-selective detector were performed on a Hewlett-Packard HP 5730A GC apparatus. Temperature programs and carrier gas flow rate were identical to those in experiments with the HP5830A. The air flow rate was 50 ml/min. The alkali bead heater voltage was held at approximately 17 V.

Atomic Absorption Analysis

Trace metal analyses were carried out with a Perkin-Elmer 5000 Atomic Absorption Spectrophotometer equipped with a graphite furnace, Perkin-Elmer HGA 2100, and a Perkin-Elmer Auto-Sampling System AS-1. Conditions under which the metal analyses were conducted are shown in Table 1.

TABLE 1. OPERATING CONDITIONS FOR ATOMIC ABSORPTION GRAPHITE FURNACE

					Temperature Program °C***		
Metal	Lamp	Wave Length (nm)	Split Width (nm)	Sample Size (ul)	Dry	Char	Atomize
As	ED*	193.6	0.7	20	110	850	2500
Cd	HC**	228.8	0.7	10	110	400	1500
Pb	HC	283.3	0.7	10	110	550	2000
Se	ED	196.0	0.7	20	110	850	2500
Zn	HC	213.9	0.7	10	110	500	2000

*Electrodeless Discharge Lamp; 1% $Ni(NO_3)_2$ was used as a fixative for both As and Se analysis.

**Hollow Cathode Lamp

***Typical times for temperature programs are: dry (40 sec), char (30 sec), and atomize (7 sec).
In all cases, a ramp mode was used between maximum dry temperature and maximum char temperature.

EXPERIMENTAL PROCEDURES

ADSORPTION OF SHALE OIL ONTO NEUTRAL ALUMINA

A chromatographic separation procedure developed for the fractionation of coal-derived solids and liquids[3] has been applied to the fractionation of the shale oil. An aliquot (3.2 g) of Paraho shale oil was dissolved in 5 ml of methylene chloride. Neutral alumina (activity I, ICN), 12 g, was then added to the solution while stirring with a glass rod to give a material the consistency of wet sand. The flask containing the mixture was subsequently put on the rotary vacuum evaporator until all the solvent had been removed and the alumina flowed smoothly. The alumina with adsorbed sample was then added to a 1.8 cm OD x 340 cm chromatography column containing 92 g of neutral alumina, activity I. The column was eluted to give the fractions shown in Table 2. Solvents were removed from the fractions by rotary evaporation until the volume was reduced to a few milliliters. A sample from each fraction was saved for GC analysis. The remaining solvent in each fraction was allowed to evaporate. Table 2 gives the weights of the collected fractions.

GAS CHROMATOGRAPHIC ANALYSIS OF SHALE OIL FRACTIONS

The fractions obtained from the alumina column fractionation of the shale oil sample have been analyzed by gas chromatography and the chromatograms are shown in Figures 2 through 8. Figure 1 indicates the relative FID and NPD responses for a series of normal hydrocarbons. While the FID shows good sensitivity to hydrocarbons, the NPD exhibits essentially no response.

TRACE METAL ANALYSIS OF SHALE OIL FRACTIONS

Analyses of lead, zinc, arsenic, cadmium, and selenium, in each of the fractions obtained from the alumina column separation of the oil, were performed using the atomic absorption-graphite furnace method. Initially, the residue from each of the fractions was dissolved in one, two or three milliliter aliquots of p-xylene. Direct injection of the solution sample into the graphite furnace, however, did not give reproducible elemental analytical results. It was necessary to take the samples to dryness again and perform a nitric acid-peroxide digestion on the residue before analysis of the aqueous digest by the atomic adsorption graphite furnace method. A minimum volume of fuming nitric acid was added to each of the fraction residues and allowed to react until a white precipitate formed. To ensure the complete oxidation of the material, 30% hydrogen peroxide was added. Each sample was then diluted to 25 ml with distilled water and the resulting solution analyzed. The results from these experiments are shown in Table 3. These values include the correction for the reagent blank containing HNO_3 and H_2O_2.

RESULTS AND DISCUSSION

Attention has focused principally on the nitrogen-and sulfur-containing compounds, since they represent the greatest potential for involvement in the mobilization of toxic inorganics by the formation of stable metal

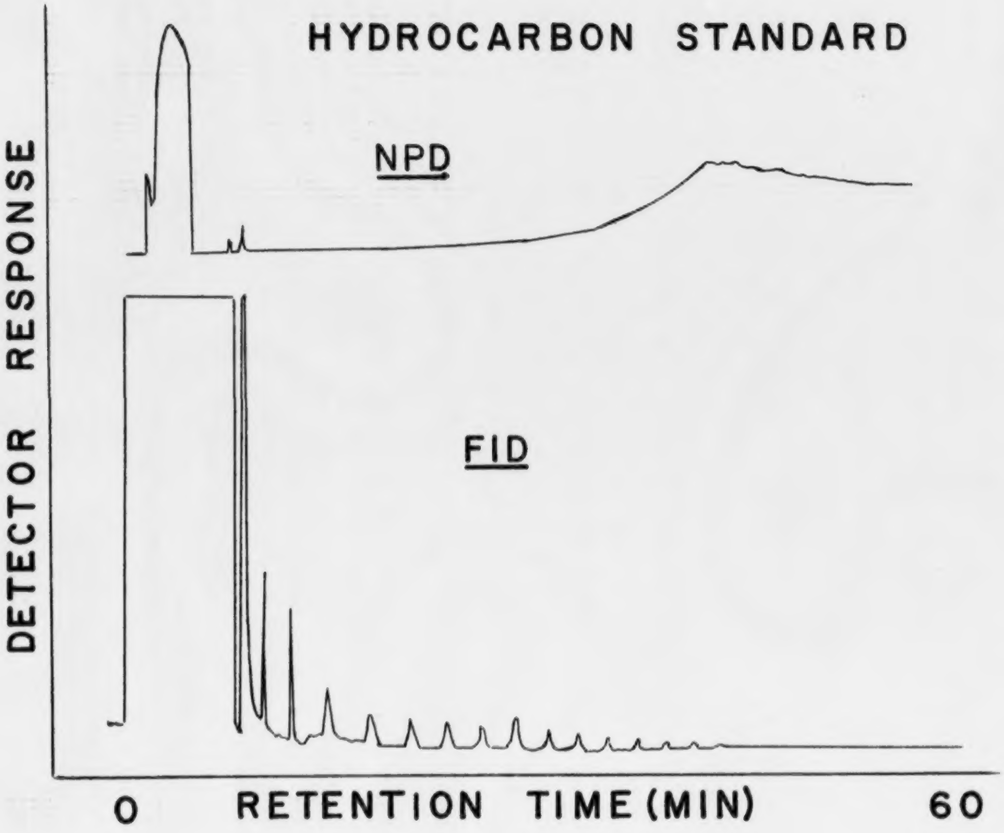

Figure 1. FID and NPD chromatograms of a standard hydrocarbon solution.

TABLE 2. ALUMINA COLUMN FRACTIONATION OF SHALE OIL*

Fraction Number	Eluant	Weight (g)
1	100 ml hexanes	0.6916
2	275 ml toluene	0.3075
3	275 ml chloroform (to the point before a large dark band began to be eluted from the column)	0.0399
4	350 ml chloroform (elution of of dark band)	1.3765
5	275 ml chloroform (volume sufficient to remove any remaining dark color)	0.1188
6	200 ml tetrahydrofuran/ethanol (9:1)	0.3295
7	250 ml methanol	0.1132
	TOTAL	2.9770 g

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*3.2 g of shale oil was introduced into the alumina column.

complexes. Since water samples were not readily available, initial investigations were conducted on samples of shale oil. Adsorption of the crude oil onto alumina followed by successive elutions with solvents of increasing polarity resulted in 7 well-resolved fractions as shown in Table 2. Individual column fractions were analyzed by GC/FID and GC/NPD. The FID chromatograms of the hexane and toluene fractions (Figures 2 and 3) show that a large proportion of the hydrocarbons and light aromatics are being eluted from the column. In the chloroform fractions, the presence of significant amounts of nitrogen-containing compounds is shown by the NPD chromatograms (Figures 4, 5, and 6). The FID response for thse fractions, however, is negligible, giving no indication of appreciable amounts of hydrocarbons. The THF/ETOH fraction shows both NPD and FID responses (Figure 7). The methanol fraction should contain compounds of high polarity; it produced relatively little FID and NPD response (Figure 8).

These results indicate that the separation achieved with the sample of shale oil is similar to that obtained with coal-derived solids and liquids on neutral alumina and appears to separate the hydrocarbons, aromatics, nitrogen and polar compounds. Analysis of these fractions for metallo-organic complexes by GC/MS/DS is currently being undertaken.

TABLE 3. ELEMENTAL CONCENTRATIONS OF A SHALE SAMPLE BEING ELUTED FROM AN ALUMINA COLUMN BY SOLVENTS WITH INCREASING POLARITY

				ug/g		
	Fraction	Cd	Pb	As	Zn	Se
1.	Hexane	0.11±0.01	≦0.2	≦0.1	≦0.7	≦0.2
2.	Toluene	0.18±0.02	3.2±0.4	≦1.6	58.0±2.4 (74.9%)	≦0.4
3.	$CHCl_3$ (three fractions combined)	0.13±0.01 (52.2%)	3.5±0.4	≦1.5 (37.1%)	2.3±0.1	≦0.3 (46.4%)
4.	THF/ETOH	0.09±0.02	4.6±0.2 (68.2%)	2.7±1.5	7.5±0.2	0.5±0.4
5.	MeOH	0.15±0.06	6.0±1.1	18.0±4.5 (32.3%)	9.5±0.7	1.5±1.1

*Numbers in parentheses refer to the percentage of an element in the principal fraction containing that element.

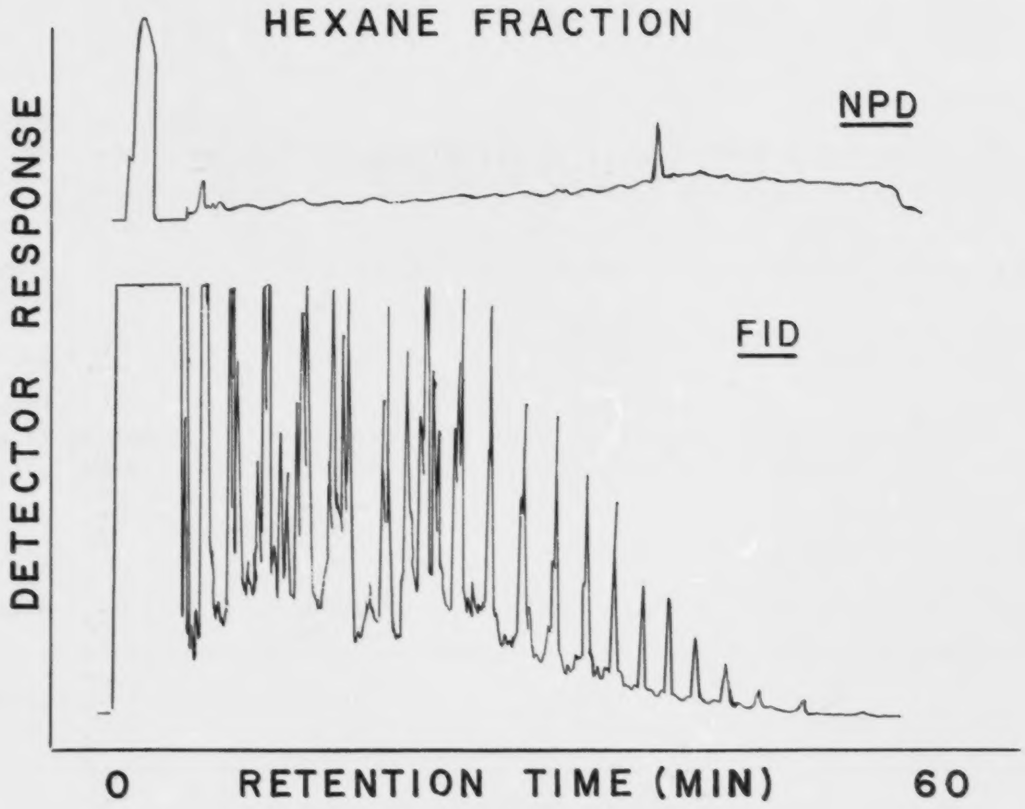

Figure 2. FID and NPD chromatograms of hexane fraction from alumina column separation of shale oil.

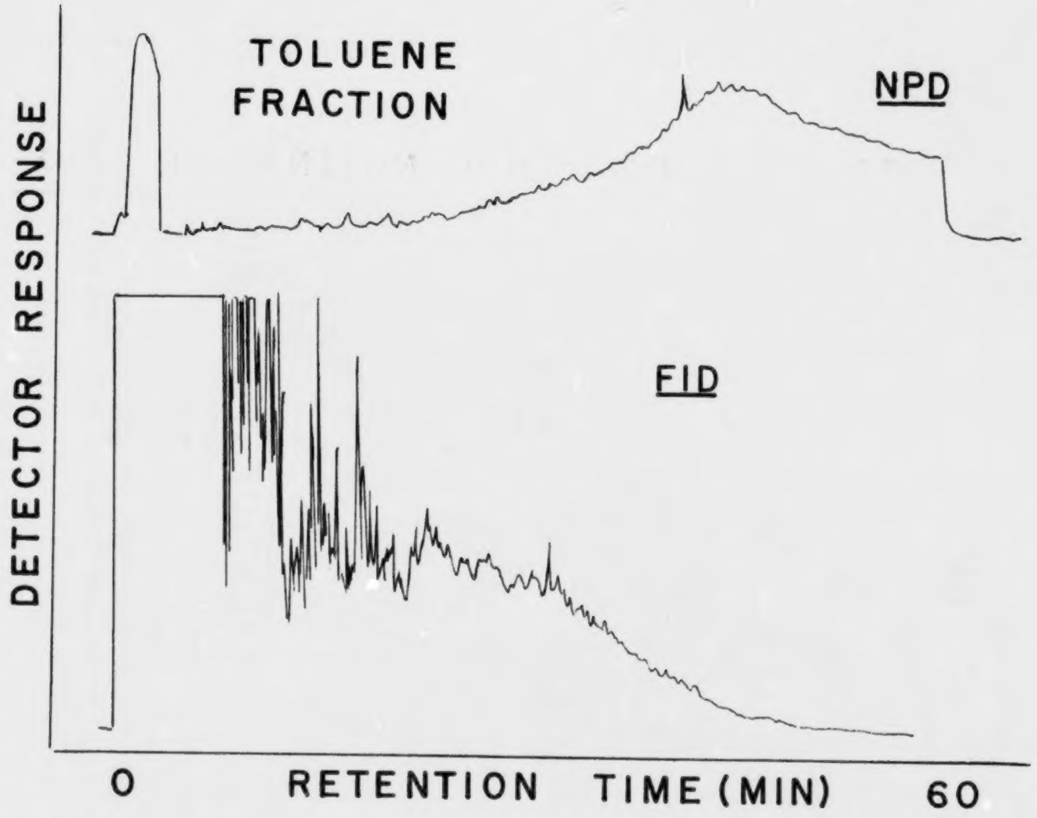

Figure 3. FID and NPD chromatograms of toluene fraction from alumina column separation of shale oil.

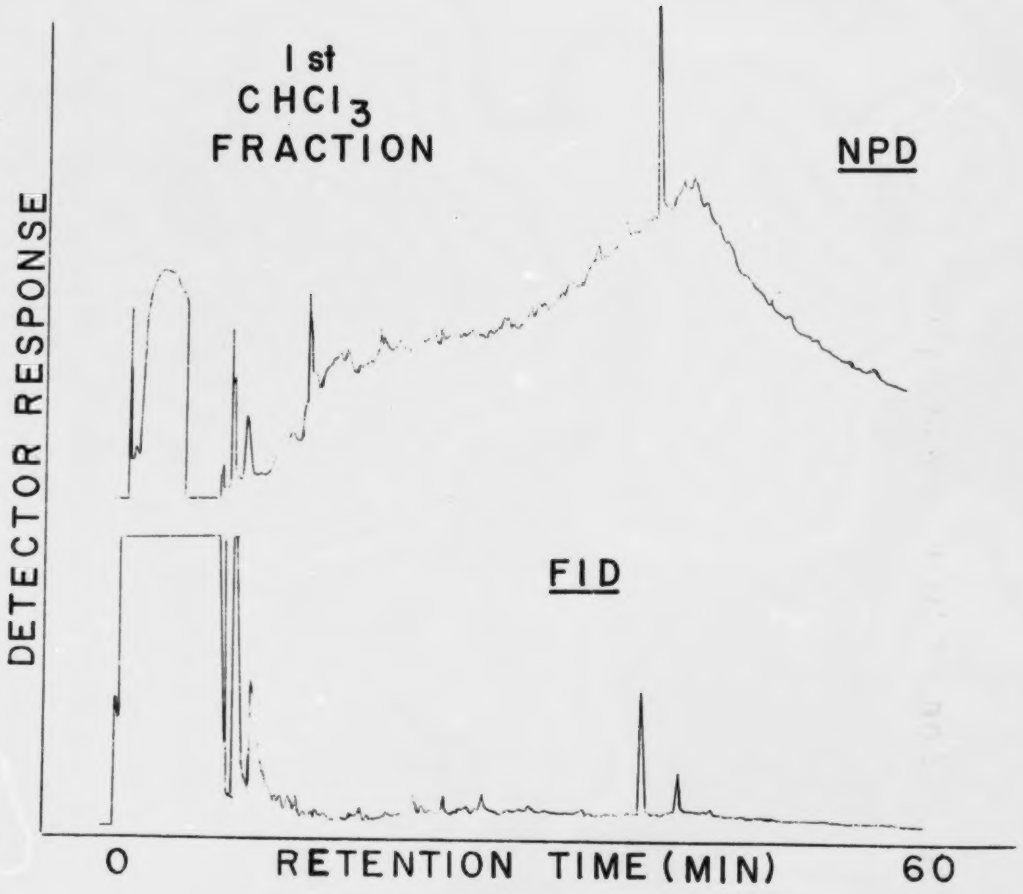

Figure 4. FID and NPD chromatograms of 1st chloroform fraction from alumina column separation of shale oil.

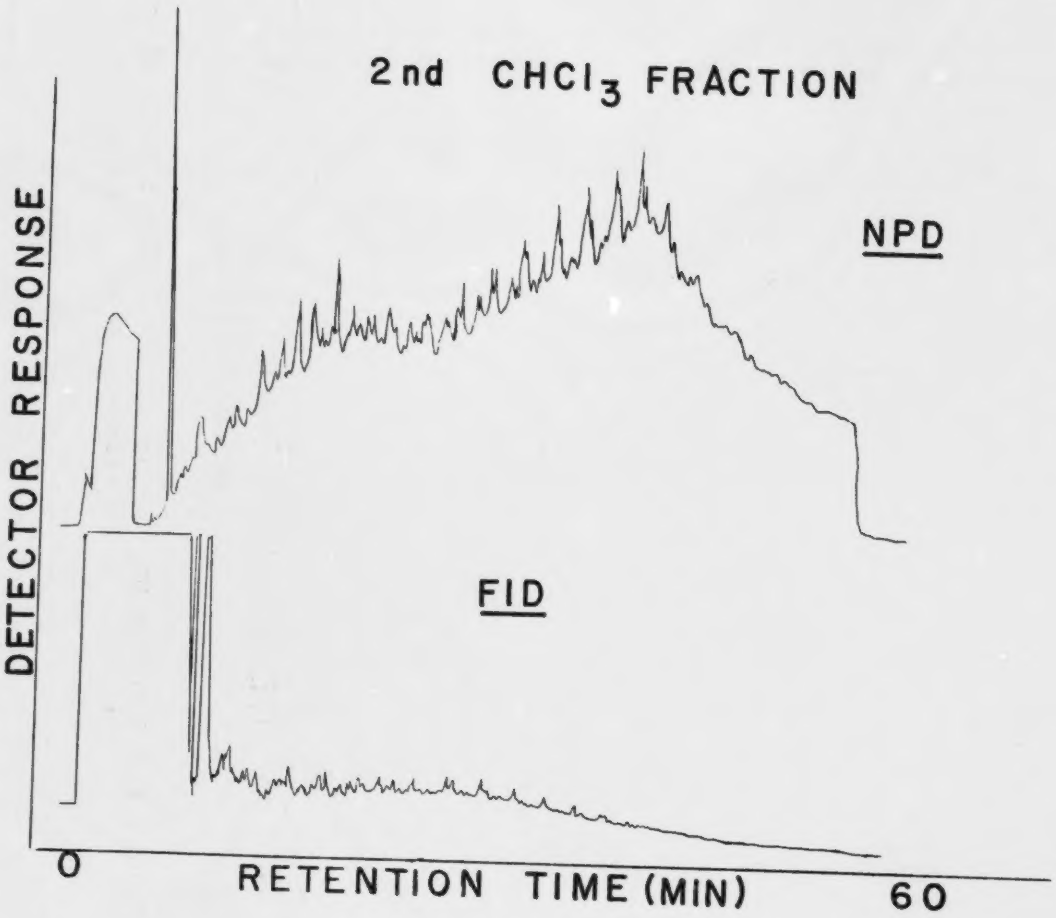

Figure 5. FID and NPD chromatograms of 2nd cholorform fraction from alumina column separation of shale oil.

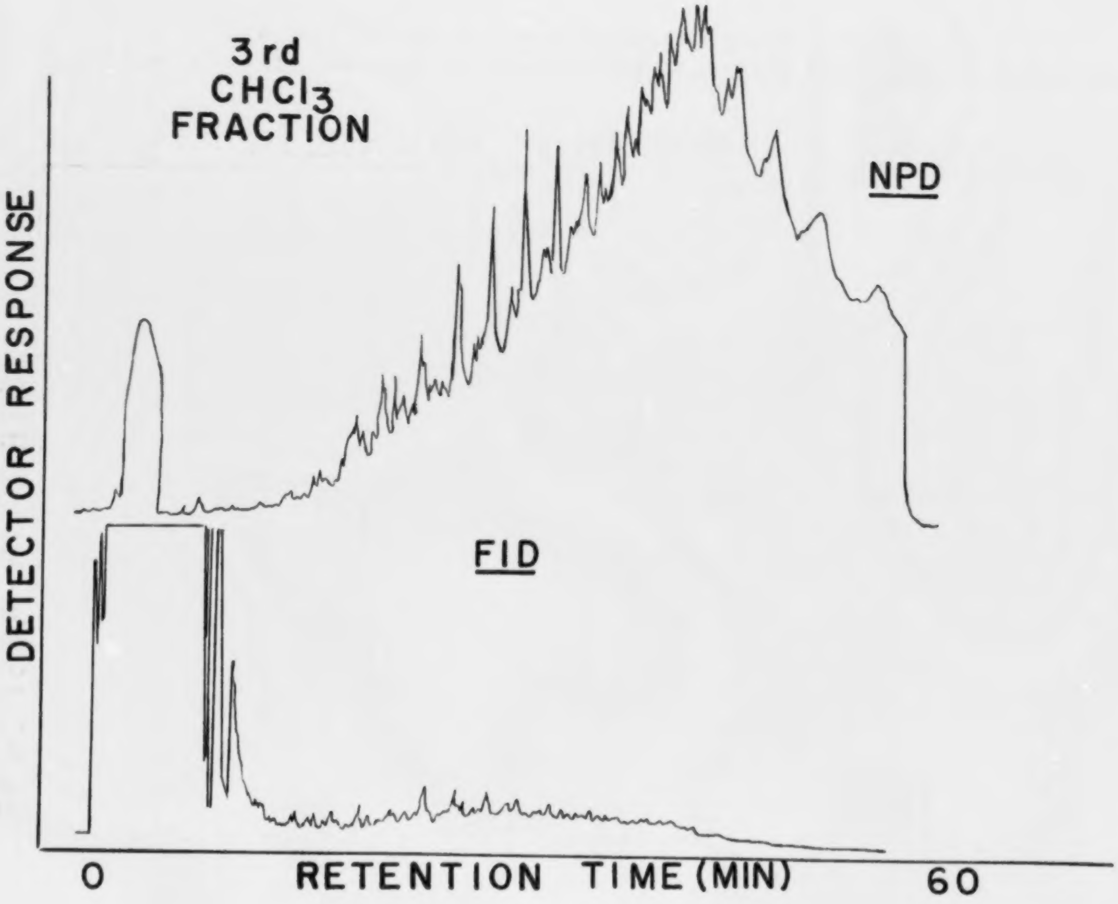

Figure 6. FID and NPD chromatograms of 3rd chloroform fraction from alumina column separation of shale oil.

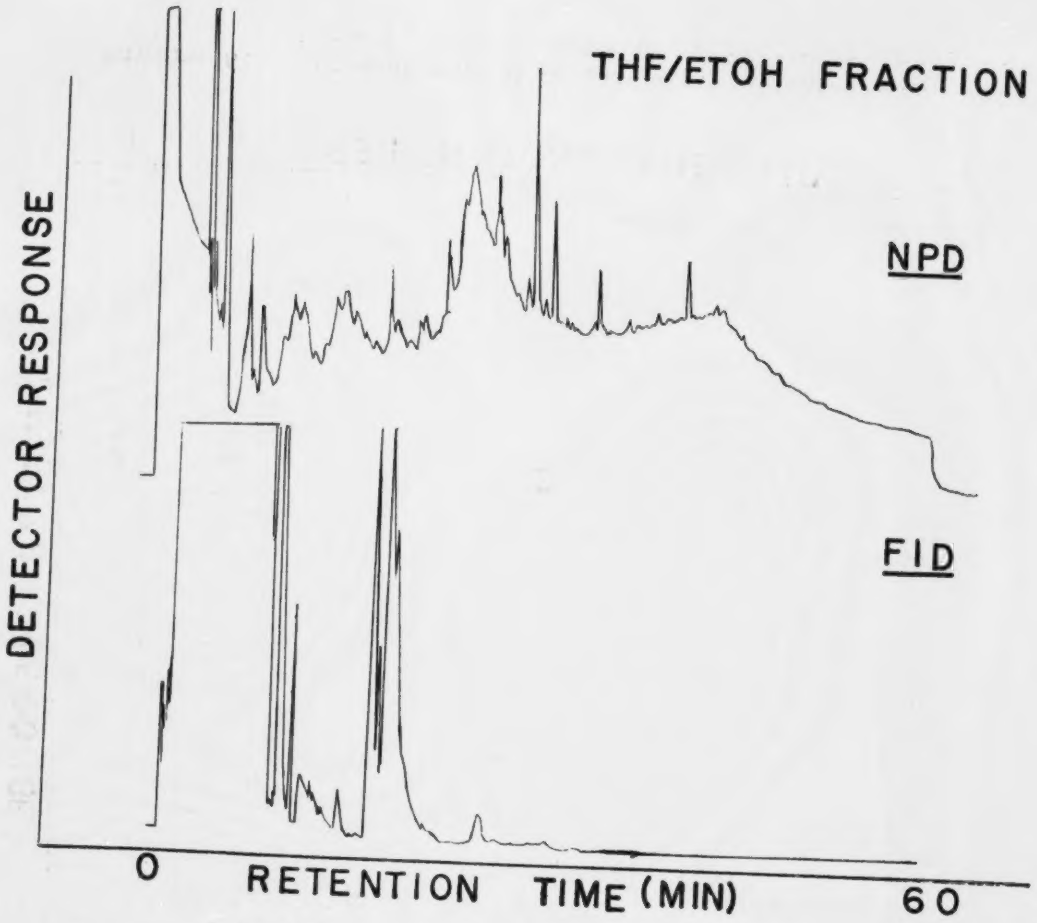

Figure 7. FID and NPD chromatograms of THF/ETOH fraction from alumina column separation of shale oil.

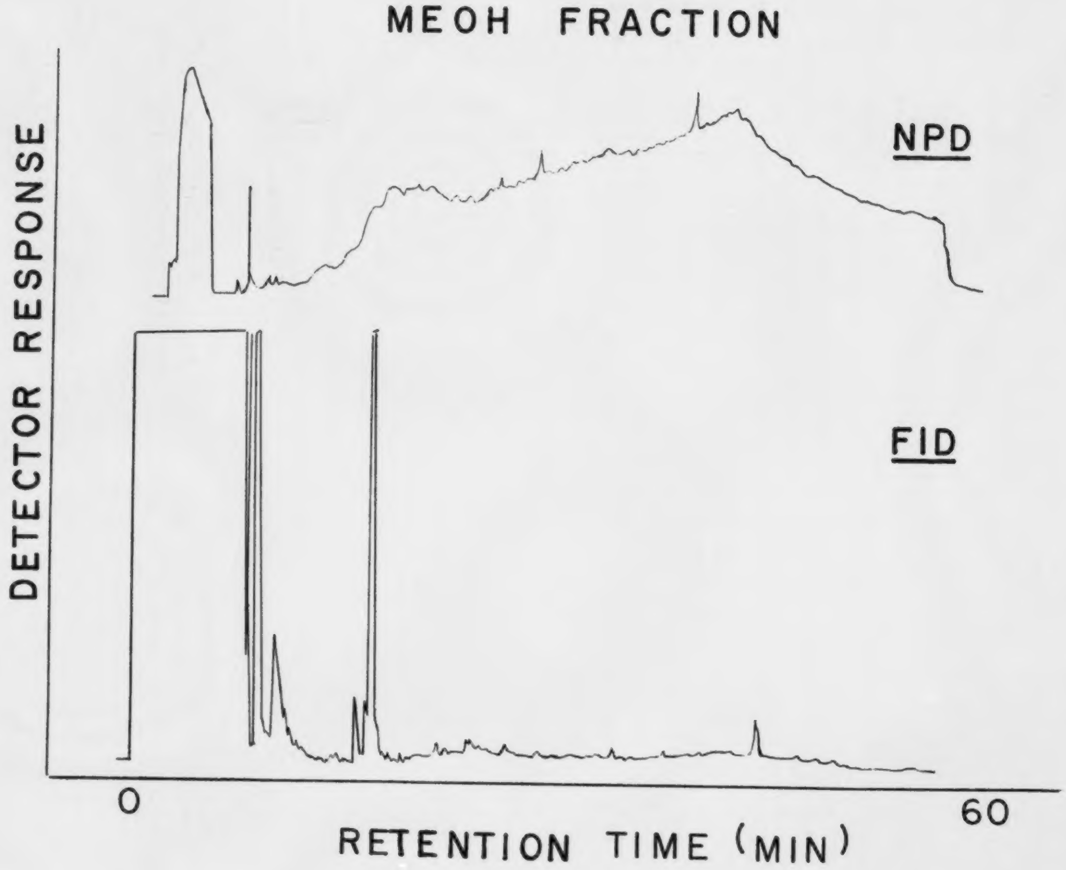

Figure 8. FID and NPD chromatograms of methanol fraction from alumina column separation of shale oil.

Since a reasonable class separation of the crude oil was achieved, it was considered important to determine the concentration of selected metal ions in each fraction. This should indicate whether certain metals had a tendency to be associated with specific classes of compounds. Trace metal analyses of the fractions were performed using the atomic absorption-graphite furnace method. Three of the elements (arsenic, cadmium and selenium) were chosen because of their toxicity, while the remaining two (lead and zinc) were chosen because their chemistries are representative of those of other elements present in the retorted shale. The results from these experiments (shown in Table 3) indicate that there is a tendency for association of the metal ion with specific fractions obtained from the separation. Most of the cadmium and selenium present in the oil sample is concentrated in the chloroform-eluted fractions, which also contain the majority of nitrogen-containing compounds. Most of the zinc is in the toluene-eluted fraction which is expected to contain the light aromatics, while most of the lead is in the THF/ETOH fraction. Arsenic appears to be distributed between the chloroform and methanol fractions. These data suggest specific metal associations with classes of organic compounds, in particular the nitrogenous bases. These bases are assumed to possess the greatest ability to form metal complexes.

In the course of these preliminary experiments separation and analysis techniques have been developed and refined. As samples of water from shale oil processing activities become available, we plan to extend these studies to learn more about possible mobilization of toxic elements by complexing agents, particularly nitrogenous bases likely to be present.

ACKNOWLEDGEMENT

We are indebted to Dr. D.W. Denney for his continued interest in this project and his helpful advice and assistance.

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RETORT WATER PARTICULATES

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Retort water may contain three types of suspended matter: oils and tars, raw and spent shale particles and a finely divided residue generally believed to be bacterial cells.[1] These particulates result in an extremely heterogeneous sample and complicated chemical analyses. Physical and chemical interactions between the retort water and these particulates, including mineral dissolution (from the spent shale particles), adsorption on the bacterial cells and oil-water solubility reactions can alter the composition of the dissolved fraction during sample storage.

The heterogeneity of unfiltered waters complicates chemical analysis. The coefficient of variation for replicate analyses may range from 20% to over 100% for many waters for analytical techniques that typically yield 10% precision. Therefore, a series of these waters was filtered to determine if this would produce a homogeneous sample that was not significantly altered in chemical composition from the original sample. Filtration of the first water produced a high density of crystals, about 50 to 100 μm in length, on the surface of the filter paper. Preliminary analyses of the particulate and dissolved fraction of the water suggested that a significant fraction of the dissolved constituents in the retort water could be removed by crystal formation. This startling result led to a more detailed investigation of the nature and origin of retort water particulates. This investigation and its results are discussed here.

EXPERIMENTAL

Eleven retort waters from Laramie Energy Technology Center's controlled-state retort were filtered, and the particulate fraction and the filtered water collected and analyzed for 17 elements by energy-dispersive x-ray fluorescence spectrometry (XRF). Retort operating conditions for these 11 waters are summarized in Table 1.

A 47 mm Millipore glass vacuum system with a fritted glass support screen and Millipore type HA 0.45 μm filter paper were used to collect particulates because they produced a uniform deposit of suspended material with a minimum of paper wrinkling. Tared filters were washed to remove readily soluble copper, iron, nickel, and zinc by filtering 100 ml of 0.06 M NH_4HCO_3 followed by 250 ml distilled water prior to filtration of the sample. The glass frit was moistened with distilled water before placing

TABLE 1. RETORT OPERATING CONDITIONS FOR LETC'S CONTROLLED-STATE RETORT

Run	Shale Type	Run Type[a]	Shale Grade (liters/ tonne)	Shale Size range (mm)	Oil Yiled, % Fischer Assay (volume basis)	Isothermal Advance Rate (m/day)	Maximum Temp. (°C)	Sweep Gas	Gas Flow Rate, Standard m^3/m^2 min.
CS-60	Colorado	I	123	3-13	46	1.83	540	100% N_2	0.12
CS-62	Utah	C	126	3-13	95	1.83	540	100% N_2	0.12
CS-63	Antrim	C	40	3-13	77	1.83	540	100% N_2	0.12
CS-64	Colorado	C	248	3-13	94	1.83	540	100% N_2	0.12
CS-65	Moroccan	C	79	3-13	88	1.83	540	100% N_2	0.12
CS-66	Colorado	C	128	3-13	91	1.83	540	75% N_2 25% steam	0.15
CS-67	Colorado	C	231	3-13	100	1.83	540	75% N_2 25% steam	0.15
CS-68	Colorado	C	119	3-13	97	1.83	540	100% N_2	0.12
CS-69	Colorado	C	118	3-13	98	1.83	760	64.5% N_2 25% steam 10.5% O_2	0.15
CS-70	Colorado	C	134	3-13	96	1.83	540	75% N_2 25% steam	0.15
CS-71	Utah	C	137	3-13	91	1.83	540	75% N_2 25% steam	0.15

[a] C = Completed run; I = Interrupted run.

the filter paper on it to prevent wrinkling during filtration. All glassware and sample bottles were washed with soap and water, rinsed with distilled water, soaked for a minimum of 12 hours in 5 N HCl, again rinsed with distilled water, dried in an 80°C oven for 4 hours and brought to room temperature before use. In addition, the glass support screen, on removal from the acid bath, was further washed by filtering 200 ml of 5 N HCl followed by 200 ml of distilled water.

The samples were removed from a 4°C refrigerator 24 hours before analysis to bring them to room temperature and shaken for 30 sec immediately before filtration. If excessive outgassing or foaming occurred, the samples were allowed to stabilize before withdrawing a sample. A sample volume sufficient to give a particulate unit mass of about 1 mg/cm^2 (5 to 25 ml) was transferred to a filtration funnel with a Pyrex pipette and filtered by vacuum at a rate of about 1 ml/sec. The filtrate was transferred to a polyethylene container and the filter paper containing the particulates was placed in a plastic petri dish in a dessicator under silica gel. The filter papers were weighed daily until a constant weight within 2% was obtained (this typically took 2 days). Two replicates of each sample were prepared in this way. The filtrate from one replicate was stored at 4°C. The filtrate from the other replicate was left at room temperature for 15 to 17 days and refiltered to investigate the effect of bacterial growth on soluble metal content. Four blanks were carried through the entire procedure.

The abundance of 17 elements was measured by energy-dispersive x-ray fluorescence spectrometry. The instrumental method has been previously described.[2] The filter paper containing the particulates was cut into 2.5 cm discs and counted for 20 or 40 min. Filtered retort waters were prepared by pipetting seven 4 μl drops of sample onto a 0.006 mm polypropylene film tightly stretched in a plastic ring. Drop location was controlled with a jig designed to produce seven concentric spots. These deposits were air dried and the samples counted for 2000 sec. Chromium was determined by neutron activation analysis,[3] and mercury was determined by Zeeman atomic absorption spectroscopy.[4] X-ray diffraction was used to identify mineral phases. Crystals were collected with tweezers under an optical microscope and adhered to a glass rod with silicon grease. A powder pattern was taken using copper Kα radiation with a nickel filter in the beam. The morphology and chemical composition of individual particles were studied using a scanning electron microscope (Advanced Metals Research Model 1000 A) equipped with an energy-dispersive XRF analyzer (EDAX).

RESULTS AND DISCUSSION

Particulate Composition

The elemental composition of the particulates and the filtered waters and the percent of the total elemental mass associated with the particulates are summarized in Table 2. This summary shows that the major elements (>0.1 mg/l) in the particulate fraction are iron, nickel, potassium, and calcium. All other measured constituents typically occur at less than 50 μg/l. The

Table 2. X-RAY FLUORESCENCE ANALYSES OF PARTICULATES AND FILTERED RETORT WATERS FROM THE CONTROLLED-STATE RETORT (mg/ℓ) (cont.)

Element	Filtered	Particulate	% Particulate	Filtered	Particulate	% Particulate	Filtered	Particulate	% Particulate	Element
	CS-67			CS-68			CS-69			
Ti	0.46 ± 0.38	<0.010	<2	0.62 ± 0.40	0.008 ± 0.007	1	0.67 ± 0.40	0.013 ± 0.010	2	Ti
V	<0.42	<0.0001	-	0.19 ± 0.07	0.017 ± 0.005	8	0.35 ± 0.28	0.018 ± 0.007	5	V
Cr	0.011 ± 0.005[a]	0.005 ± 0.003	31	0.050 ± 0.007[a]	0.004 ± 0.003	7	0.061 ± 0.006[a]	0.011 ± 0.005	15	Cr
Mn	<0.21	<0.004	<0.10	0.22 ± 0.14	<0.004	<2	<0.21	0.013 ± 0.004	-	Mn
Fe	1.07 ± 0.14	0.140 ± 0.006	12	3.22 ± 0.20	0.178 ± 0.008	5	4.35 ± 0.56	0.157 ± 0.007	3	Fe
Ni	1.26 ± 0.08	0.023 ± 0.002	2	3.61 ± 0.18	0.122 ± 0.006	3	1.52 ± 0.37	0.54 ± 0.03	26	Ni
Ga	<0.06	<0.001	-	0.07 ± 0.04	<0.001	<1	0.06 ± 0.04	<0.002	<3	Ga
As	3.50 ± 0.18	0.0105 ± 0.0008	0.3	16.9 ± 0.8	0.054 ± 0.003	0.3	7.32 ± 0.93	0.033 ± 0.002	0.5	As
Se	1.25 ± 0.06	0.0090 ± 0.0008	1	0.71 ± 0.04	0.0034 ± 0.0006	0.5	0.60 ± 0.06	0.074 ± 0.004	12	Se
Br	0.38 ± 0.04	<0.001	<0.3	0.16 ± 0.06	<0.002	<1	<0.09	<0.002	-	Br
Rb	0.29 ± 0.06	<0.002	<1	0.60 ± 0.06	0.0020 ± 0.0012	0.3	0.50 ± 0.06	0.0020 ± 0.0016	0.4	Rb
Sr	0.10 ± 0.08	<0.002	<2	0.21 ± 0.08	0.0017 ± 0.0014	1	0.21 ± 0.08	0.0035 ± 0.0022	2	Sr
Y	<0.15	0.0023 ± 0.0018	-	<0.15	<0.003	-	<0.15	<0.004	-	Y
Hg	0.090 ± 0.009	0.0099 ± 0.0016	5	0.134 ± 0.014	0.021 ± 0.002	11	0.024 ± 0.013	0.079 ± 0.004	77	Hg
Pb	<0.24	0.0028 ± 0.0026	-	<0.24	0.007 ± 0.003	-	<0.24	0.0075 ± 0.0042	-	Pb
K	4.46 ± 2.66	0.038 ± 0.029	1	43.4 ± 3.0	0.20 ± 0.03	0.5	36.7 ± 1.0	0.078 ± 0.042	0.2	K
Ca	5.76 ± 0.94	0.075 ± 0.017	1	20.0 ± 6.6	0.16 ± 0.02	1	18.8 ± 2.7	0.28 ± 0.03	1	Ca
Solids		241 ± 30			219 ± 78			375 ± 1		Solids
	CS-70			CS-71						
Ti	0.81 ± 0.40	<0.03	<4	<0.57	<0.014	-				
V	0.40 ± 0.28	0.018 ± 0.013	5	0.32 ± 0.26	0.008 ± 0.007	2				
Cr	0.055 ± 0.006	0.015 ± 0.009	21	0.043 ± 0.004[a]	<0.007	<14				
Mn	<0.21	<0.010	<0.04	<0.21	0.0076 ± 0.0036	-				
Fe	4.36 ± 0.22	0.135 ± 0.008	3	3.29 ± 0.16	0.23 ± 0.01	7				
Ni	1.52 ± 0.08	0.50 ± 0.03	25	1.94 ± 0.10	0.021 ± 0.003	1				
Ga	0.05 ± 0.04	<0.003	<6	0.05 ± 0.04	<0.002	<4				
As	7.48 ± 0.37	0.059 ± 0.023	1	4.57 ± 0.23	0.025 ± 0.003	1				
Se	0.57 ± 0.04	0.101 ± 0.006	15	0.33 ± 0.04	0.0017 ± 0.0010	1				
Br	<0.09	<0.004	-	0.14 ± 0.04	<0.002	<1				
Rb	0.50 ± 0.06	0.0069 ± 0.0031	1	0.17 ± 0.06	<0.002	<1				
Sr	0.21 ± 0.08	0.0077 ± 0.0040	4	0.21 ± 0.08	0.0083 ± 0.0022	4				
Y	<0.15	0.0068 ± 0.0048	-	<0.15	<0.004	-				
Hg	0.025 ± 0.007	0.073 ± 0.005	74	0.048 ± 0.002	0.0019 ± 0.0003	4				
Pb	<0.24	0.011 ± 0.008	-	<0.21	<0.006	-				
K	36.1 ± 2.9	0.24 ± 0.09	1	18.7 ± 2.7	0.077 ± 0.043	0.4				
Ca	23.8 ± 1.2	0.34 ± 0.05	1	14.0 ± 1.0	0.93 ± 0.10	6				
Solids		451 ± 32			203 ± 46	Solids				

[a] Neutron activation analysis

Table 2. X-RAY FLUORESCENCE ANALYSES OF PARTICULATES AND FILTERED RETORT WATERS FROM THE CONTROLLED-STATE RETORT (mg/ℓ)

Element	Filtered	Particulate	% Particulate	Filtered	Particulate	% Particulate	Filtered	Particulate	% Particulate	Element
	CS-60			CS-62			CS-63			
Ti	<0.60	<0.053	-	<0.60	<0.056	-	0.69 ± 0.40	0.030 ± 0.011	4	Ti
V	<0.42	<0.037	-	<0.42	<0.040	-	0.49 ± 0.28	<.040		V
Cr	1.74 ± 0.22	0.15 ± 0.02	8	0.57 ± 0.01[a]	0.43 ± 0.02	43	0.09 ± 0.01[a]	0.058 ± 0.006	39	Cr
Mn	0.23 ± 0.16	0.03 ± 0.01	14	<0.21	0.065 ± 0.018	-	0.31 ± 0.14	0.022 ± 0.005	7	Mn
Fe	19.2 ± 0.9	4.32 ± 0.21	18	6.60 ± 0.33	8.73 ± 1.35	57	1.30 ± 0.14	1.43 ± 0.07	52	Fe
Ni	2.06 ± 0.10	3.38 ± 0.16	62	1.34 ± 0.08	9.32 ± 0.14	87	0.98 ± 0.08	0.031 ± 0.003	3	Ni
Ga	0.05 ± 0.04	<0.006	<11	0.06 ± 0.04	<0.006	<9	0.06 ± 0.04	<0.003	<5	Ga
As	6.04 ± 0.30	0.12 ± 0.01	2	6.22 ± 0.31	0.130 ± 0.006	2	1.82 ± 0.09	0.016 ± 0.002	1	As
Se	0.37 ± 0.04	0.032 ± 0.004	8	0.47 ± 0.04	0.043 ± 0.004	8	0.51 ± 0.04	0.004 ± 0.001	1	Se
Br	0.10 ± 0.06	<0.006	<6	0.15 ± 0.06	<0.007	<4	0.58 ± 0.04	<0.002	<0.3	Br
Rb	0.28 ± 0.06	<0.009	<3	0.15 ± 0.06	<0.009	<6	1.21 ± 0.06	0.004 ± 0.002	0.3	Rb
Sr	0.41 ± 0.08	0.025 ± 0.008	<6	<0.12	<0.012	-	0.20 ± 0.08	0.168 ± 0.008	46	Sr
Y	<0.15	<0.014	-	<0.15	<0.014	-	<0.15	0.003 ± 0.003	-	Y
Hg	<0.001	0.029 ± 0.008	~100	<0.001	0.051 ± 0.009	~100	0.025 ± 0.006	0.055 ± 0.003	69	Hg
Pb	<0.24	0.02 ± 0.01	-	<0.24	0.025 ± 0.015	-	<0.24	0.022 ± 0.004	-	Pb
K	18.8 ± 2.8	<0.24	<1	<4.11	<0.23	-	163 ± 8	0.76 ± 0.06	0.5	K
Ca	13.1 ± 1.0	13.4 ± 0.6	51	5.75 ± 0.98	0.43 ± 0.09	7	5.97 ± 1.2	8.48 ± 0.42	59	Ca
Solids		2190 ± 160			2984 ± 123			341 ± 41		Solids
	CS-64			CS-65			CS-66			
Ti	<0.57	<0.01	-	<0.60	0.068 ± 0.013	-	<0.60	0.017 ± 0.012	-	Ti
V	<0.39	0.008 ± 0.006	-	<0.42	0.020 ± 0.009	-	<0.42	0.022 ± 0.009	-	V
Cr	0.028 ± 0.005[a]	<0.007	<20	0.24 ± 0.20	0.072 ± 0.007	23	0.038 ± 0.006[a]	<0.009	<19	Cr
Mn	0.20 ± 0.14	<0.005	<2	0.22 ± 0.14	0.014 ± 0.005	6	0.27 ± 0.14	<0.007	<3	Mn
Fe	1.91 ± 0.14	0.108 ± 0.005	5	0.42 ± 0.12	1.60 ± 0.07	79	1.59 ± 0.25	0.39 ± 0.02	20	Fe
Ni	2.29 ± 0.11	0.036 ± 0.002	2	2.51 ± 0.13	0.094 ± 0.005	4	2.74 ± 1.15	0.29 ± 0.01	10	Ni
Ga	0.05 ± 0.04	<0.002	<4	0.07 ± 0.04	<0.002	<3	0.05 ± 0.04	<0.002	<4	Ga
As	3.66 ± 0.18	0.023 ± 0.001	1	2.47 ± 0.12	0.016 ± 0.001	1	14.1 ± 2.3	0.055 ± 0.003	0.4	As
Se	0.35 ± 0.04	0.003 ± 0.001	1	5.79 ± 0.29	0.045 ± 0.002	1	0.49 ± 0.08	0.007 ± 0.001	1	Se
Br	0.53 ± 0.06	<0.002	<0.4	0.61 ± 0.06	<0.002	<0.3	0.07 ± 0.06	<0.002	<3	Br
Rb	0.28 ± 0.06	<0.002	<0.7	0.34 ± 0.06	0.0047 ± 0.0020	1	0.66 ± 0.09	0.004 ± 0.002	1	Rb
Sr	<0.12	<0.003	-	0.12 ± 0.08	0.032 ± 0.003	21	0.33 ± 0.08	0.007 ± 0.003	2	Sr
Y	0.12 ± 0.10	<0.004	<3	<0.15	<0.005	-	<0.15	<0.005	-	Y
Hg	0.181 ± 0.005	0.015 ± 0.002	8	0.253 ± 0.025	0.067 ± 0.004	21	0.127 ± 0.014	0.033 ± 0.003	21	Hg
Pb	<0.24	0.006 ± 0.004	-	0.19 ± 0.18	0.006 ± 0.005	3	<0.24	0.007 ± 0.005	-	Pb
K	<4.0	<0.06	-	60.3 ± 3.1	0.33 ± 0.05	1	53.6 ± 5.1	0.23 ± 0.05	0.4	K
Ca	4.13 ± 0.92	<0.03	<1	6.2 ± 1.1	3.19 ± 0.15	34	22.9 ± 1.3	0.57 ± 0.04	2	Ca
Solids		248 ± 33			1503			337 ± 17		Solids

[a] Neutron activation analysis

Table 3. X-RAY FLUORESCENCE ANALYSES OF PARTICULATES FROM FIRST AND SECOND FILTRATION OF WATERS CS-66, CS-68 AND CS-69 (ng/ml)

Element	CS-66		CS-68		CS-69	
	First Filtration	Second Filtration[a]	First Filtration	Second Filtration[a]	First Filtration	Second Filtration[a]
As	54.6 ± 2.7	80.2 ± 4.0	54.1 ± 2.7	84 ± 4	33.1 ± 1.7	81.6 ± 4.0
Br	<2.4	<3.3	<1.5	<2.4	<2.4	<4.5
Ca	573 ± 35	334 ± 34	156 ± 17	<43	282 ± 26	2990 ± 150
Cr	<8.7	9.9 ± 6.0	4.1 ± 3.2	<8.4	10.9 ± 4.8	14.6 ± 11.6
Cu	5.2 ± 3.0	29.1 ± 4.0	41.4 ± 2.1	230 ± 11	63.4 ± 3.4	<13.5
Fe	390 ± 18	202 ± 10	178 ± 8	168 ± 8	157 ± 7	83.5 ± 43
Ga	<2.1	<2.1	<1.2	<2.1	<1.8	<3.9
Hg	33.2 ± 3.4	142 ± 7	20.9 ± 1.8	11.2 ± 2.8	78.6 ± 3.9	14.3 ± 6.0
K	228 ± 54	374 ± 55	201 ± 30	276 ± 52	78.3 ± 42.2	291 ± 106
Mn	<6.9	<6.9	<3.6	<6.6	12.8 ± 4.0	12.7 ± 9.0
Ni	294 ± 14	977 ± 48	122 ± 6	195 ± 9	542 ± 27	225 ± 11
Pb	6.8 ± 4.8	<7.5	6.7 ± 2.6	<7.5	7.5 ± 4.2	<14.7
Rb	4.0 ± 2.0	4.1 ± 2.0	2.0 ± 1.2	2.5 ± 2.0	2.0 ± 1.6	6.1 ± 4.0
Se	6.5 ± 1.2	32.7 ± 1.6	3.4 ± 0.6	5.3 ± 1.2	73.7 ± 3.7	19.7 ± 2.6
Sr	6.5 ± 2.6	6.8 ± 2.6	1.7 ± 1.4	<3.9	3.5 ± 2.2	29.0 ± 5.4
Ti	17 ± 12	<18	7.6 ± 6.6	<18	13.3 ± 9.8	<35.1
V	22 ± 9	<13	17.0 ± 4.8	9.6 ± 8.6	18.0 ± 7.2	<25.2
Y	<4.8	<4.8	<2.7	<4.5	<3.9	<9.3
Zn	68.6 ± 3.4	13.0 ± 2.2	114 ± 5	133 ± 6	156 ± 7	9.6 ± 4.8
Total Solids	337 ± 17	257 ± 16	219 ± 78	153	375 ± 1	228 ± 1

[a] The second filtration was performed on the filtrate from the first filtration after it had been maintained at room temperature for 15 to 17 days.

Table 4. X-RAY FLUORESCENCE ANALYSES OF THE TOP AND BOTTOM 1 mm OF LIQUID IN WATERS CS-64, CS-65 AND CS-67 AFTER STORAGE FOR 1 YEAR AT ROOM TEMPERATURE (ng/ml)

	CS-64		CS-65		CS-67	
Element	TOP	BOTTOM	TOP	BOTTOM	TOP	BOTTOM
As	4.6 ± 0.2	5.5 ± 0.2	3.1 ± 0.2	4.9 ± 0.2	5.4 ± 0.2	4.3 ± 0.2
Br	0.4 ± 0.1	0.6 ± 0.1	0.6 ± 0.1	1.2 ± 0.2	0.5 ± 0.1	0.5 ± 0.1
Fe	1.1 ± 0.4	2.5 ± 0.4	<0.5	0.7 ± 0.4	1.0 ± 0.4	1.6 ± 0.4
Ge	<0.2	0.3 ± 0.1	<0.2	0.4 ± 0.1	<0.2	0.3 ± 0.1
Hg	0.072 ± 0.011	0.75 ± 0.014	0.059 ± 0.005	0.78 ± 0.08	0.065 ± 0.008	0.51 ± 0.10
Ni	2.2 ± 0.2	4.9 ± 0.3	2.0 ± 0.2	5.5 ± 0.3	1.3 ± 0.2	3.2 ± 0.3
Rb	0.3 ± 0.2	0.3 ± 0.2	0.4 ± 0.2	0.6 ± 0.2	0.3 ± 0.2	0.4 ± 0.2
Se	0.4 ± 0.1	0.5 ± 0.1	4.5 ± 0.2	12.3 ± 0.4	2.0 ± 0.2	1.8 ± 0.1
Sr	<0.3	<0.3	0.3 ± 0.2	0.3 ± 0.2	0.2 ± 0.2	<0.3

fraction of the total elemental mass present in the particulates (% particulate) is typically less than, or about, 1% for potassium, arsenic, selenium, bromine, and rubidium. The percent particulate is significantly greater than 1% for iron, chromium, mercury, and nickel in most samples.

Three of the filtered samples (CS-66, -68 and -69) exhibited remarkable visual changes during storage at room temperature. All three samples became turbid and a finely divided deposit collected at the bottom of each container. Similar, but less marked behavior was noted in all filtrates left at room temperature. No visual changes occurred in the samples stored at <4°C. These three samples were filtered after 15 to 17 days of storage at room temperature and the particulates analyzed. The elemental composition of particulates collected from these three waters during the first and second filtration are compared in Table 3. This table shows that there is a significant concentration of solids and of all of the elements in the particulate fraction from the second filtration. The ratio of the solids from the second to those from the first filtration is 0.69 ± 0.08, i.e., 69% of the mass collected during the first filtration was again collected during the second. This could only occur if the first filtration was not successful in removing all the particulates that can be captured by a 0.45 µm filter (not likely) or if significant bacterial activity occurred in the sample. The visual appearance of the samples (sediment at the bottom of the container) plus the work of Farrier[1] support the conclusion that the high solids level obtained on the second filtration is largely due to bacterial growth. Microscopic examination of the sediment from one of the waters revealed rod-shaped structures similar to those reported by Farrier.[1]

The effect of this sediment on the concentration of nine elements was examined by sampling the top and bottom 1 mm of three waters that had been stored under ambient conditions for about 1 year. The results of these determinations, shown in Table 4, indicate that there is a concentration gradient between the top and bottom of the sample container for mercury, nickel, arsenic, iron, germanium, bromine, and selenium. The majority of the mercury and varying amount of the other elements is at the bottom of the container in the sediment. This suggests that the bacterial cells remove these elements from solution. The high percent particulate values for mercury and nickel in Table 2 support this.

The uniformly high level of most of the elements measured in the particulates from the second filtration (Table 3) cannot be entirely explained by removal by bacteria. As will be seen in discussion to follow, precipitation during during filtration is an important factor.

Particle Morphology

The morphology and chemical composition of individual particles present in the particulate fraction of each water are presented in Figures 1-12. This series of figures presents scanning electron micrographs of particulates from each water and x-ray spectra of individual particles shown in the micrographs. Since only a small area is represented by each micrograph, it should not be assumed that the types of particles present are limited to those shown.

A visual classification of the particles reveals that there are two types present: crystals and amorphous solids. These particles are imbedded in a uniform background of spongy or scaly material. The only element detected in the matte material is sulfur (carbon and nitrogen are likely to be present but cannot be detected by EDAX). The amorphous particles are rounded (see Figures 4 and 5) and their chemical composition is silicon-aluminum (calcium, potassium, iron, sodium). The crystalline particles are varied in shape and are composed of iron, calcium, magnesium or nickel. The particles range in size from a micron or less to about 100 μm.

The rounded amorphous particles are hypothesized to be spent shale particles. This is supported by their composition and their similarity to individual particles of spent shale and is consistent with the mineral composition of spent shale particles.[5]

The crystalline particles are highly varied in both form and chemical composition. Three rather striking crystal types were obtained. Filtration of water CS-62 (from an inert gas run using Utah shale) produce a high density of cubic crystals (3μm sides) of iron and nickel (see Figure 2). The associated anion is unknown. The small size of the crystals prevented their identification by x-ray diffraction techniques. The unique formation of nickel-iron crystals during filtration of water CS-62 is consistent with the chemical composition of unfiltered water. This water contains 10.7 mg/l of nickel, 15.3 mg/l of iron and 2.8% sulfur. These are the highest values of these three elements found in any of the 11 waters.

Filtration of water CS-63 (from an inert gas run using Antrim shale) produced a high density of long needle-like crystals in a radial array with a diameter of about 7 μm (Figure 3). The simultaneous presence of high levels of strontium, magnesium, potassium and sulfur distinguish this water from others in the set studied. EDAX analyses indicate that the only cation present is calcium. X-ray diffraction on individual crystals identified the mineral phase as aragonite. Solubility calculations support the x-ray diffraction identification. Water CS-63 is supersaturated with respect to both aragonite and calcite. The crystallization of aragonite is favored by the presence of small amounts of barium, strontium, magnesium or lead salts and $CaSO_4$, by rapid precipitation and by relatively high concentrations of reactants.[6] All of these conditions are met for water CS-63.

Water CS-69 (from a steam combustion run using Colorado shale) produced a high density of prismoidal crystals (30 μm side) in which the predominant cation is magnesium (Figure 9). These larger crystals coexist with clusters of microcrystals of magnesium and sulfur. The larger crystals are probably magnesium carbonate and the microcrystals are probably gypsum ($CaSO_4 \cdot 2H_2O$). Solubility calculations indicate water CS-69 is supersaturated with respect to magnesite ($MgCO_3$), nesquehonite ($MgCO_3 \cdot 3H_2O$) and hydromagnesite ($Mg_4(CO_3)_3(OH_2) \cdot 3H_2O$). Other work[6] indicates that precipitation at ordinary temperature and pressure gives either nesquehonite or a basic carbonate such as hydromagnesite. Thus, the larger crystals are likely one of these forms of magnesium carbonate. X-ray diffraction on individual crystals failed to identify the mineral phase. The crystals apparently decomposed between the initial filtration and the x-ray diffraction work (~ one year). This was verified by re-examining the deposits by scanning electron microscope. The crystals present in CS-69 had been replaced by deposits similar to those shown in the micrographs in Figures 1 and 10 suggesting that both of these deposits may have contained crystalline material at one time.

A number of other particles with a predominance of a single cation, either calcium, magnesium, iron, aluminum or silicon, was also identified. The density of these other particles was lower and their structure was not readily discernible from the data at hand. Examples of these other particles include: (1) concave particles with dark centers in which iron is the predominant cation (particle 2A in Figure 3 and particle 2D in Figure 7), (2) rounded amorphous particles in which silicon, likely as SiO_2, is the predominant cation (all particles in Figure 5, and particle 1A in Figure 6), and (3) obscured particles in which aluminum is the predominant cation (particle 3A in Figure 10 and particle 1C in Figure 9).

Other particles were observed in which no element, except sulfur, was founded (indicating a composition of elements lighter than aluminum). The sulfur, in all cases, is attributed to the background matte and not the particle. Examples of these crystals are seen in Figure 2 (particles 1A, 2A, 1C-4C) and Figure 6 (particles 4A, 5A). Based on the composition of retort waters, these particles may be such compounds as NH_4HCO_3, $NH_4(CO_3)_2$ or salts of organic acids, such as $(NH_4)_2C_2O_4 \cdot H_2O$.

Particle Formation Mechanisms

Four mechanisms are adequate to explain the origin and composition of retort water particulates. These four mechanisms are: (1) oil and spent shale particle suspension during retorting, (2) evaporation of an equivalent 1 mm deep layer of retort water from the filter surface, (3) crystal formation during filtration due to CO_2 outgassing and (4) bacterial removal. These mechanisms explain the following major observations:

1. The particulate fraction consists of a uniform fibrous matte in which individual crystalline or amorphous particles are embedded.

2. The concentration of 19 elements and solids in particulates collected during two successive filtrations of the same water are similar.

3. The elements calcium, magnesium, iron, silicon, aluminum, potassium, sodium, nickel, barium, and chromium are localized in individual particles and are the major elements in the particulates. The elements arsenic, selenium, rubidium, strontium, mercury, gallium, lead, yttrium, titanium, and manganese are uniformly distributed in the matte material and occur at low levels, typically less than 10 μg/l.

4. One percent or less of the total mass of potassium, arsenic, selenium, bromine, and rubidium and considerably more than 1% of the iron, nickel, mercury, and chromium present in the unfiltered water occur in the particulate fraction.

5. A significant concentration gradient may exist between the top and bottom of an unrefrigerated sample for the elements mercury, nickel, germanium, arsenic, bromine, iron, and selenium.

6. The elemental composition and morphology of the amorphous particles are similar to spent shale. Crystalline particles are typically composed of either calcium, magnesium or iron.

Suspension of Spent Shale Fines and Oil--

Oil shale becomes friable during retorting due to the removal of kerogen from the mineral matrix. Bed settling and errosion by hot combustion gases may release spent shale fines which are entrained in the gases and either settle out or are entrapped during the condensation of oil and water vapors. Spent shale fines are composed of akermanite, diopside, calcite, albite, analcime and other minerals; the principal elements are silicon, aluminum, calcium, iron, magnesium, and sodium.[5] The morphology and composition of these fines are very similar to the silicon-aluminum-(calcium, magnesium, iron, sodium) particles that are present in most of the waters. The round shape of these particles, suggesting heat treatment, also supports the theory that they are spent shale fines.

Oil and water condense out of the gas phase and move down the packed bed as an emulsion. After separation of these phases, a small amount of oil remains in the water phase. This oily material is removed during filtration of the sample and collects as a spongy fibrous matte on the filter paper. This is supported by its visual appearance, texture and odor and by the presence of a strong sulfur peak in the x-ray spectrum of the backgrounds of most of the samples. Calculations indicate that this oil does not significantly contribute to the measured elemental abundances in retort water particulates (<1%).

Surface Evaporation--

Since the organic matte (oil and bacterial cells) and filter paper are hygroscopic, some of the filtered water is retained following filtration. When this retained water is evaporated, the dissolved ions present in it are deposited on the filter paper. If it is assumed that the equivalent moisture film thickness is 1 mm, then about 0.14 ml of water is retained on the filter paper for a deposit with a diameter of 42 mm. If 25 ml of sample are filtered, then 0.55% of the total elemental mass in the unfiltered sample will be deposited approximately uniformly. This is within an order of magnitude of the amount of potassium, arsenic, selenium, bromine, rubidium and titanium found in all of the particulates for which 25 ml were filtered. Five ml of waters (CS-60 and CS-62 and 10 ml of water CS-69 were filtered.

Thus, about 1.5% and 3% of the elemental mass in the unfiltered sample should be deposited for the 10 ml and 5 ml samples, respectively. This is consistent within an order of magnitude (see Table 2) with the particulate data and the elemental abundance data for potassium, arsenic, selenium, bromine, and rubidium.

Surface evaporation of a 1 mm layer is also supported by the fact that the particulate composition in two successive filtrations is similar and by the fact that the elements occurring at low levels in the particulates (i.e., about the right order of magnitude to have been deposited by evaporation of a 1 mm layer) are not localized in the particulates with the exception of potassium (occurs in spent shale fines).

Precipitation--

The crystals noted in some particulates probably form during filtration. If these crystals were formed during or immediately subsequent to retorting, they would likely redissolve as the solubility of carbonates decreases at elevated temperatures.

Most retort waters are supersaturated with respect to a number of mineral phases such as calcite, aragonite, magnesite and siderite. However, the high concentration of organics in these waters may increase the solubility relative to that predicted for infinitely dilute solutions. During filtration, CO_2 is stripped out of solution. This drives the reaction to the left and metal carbonates ($MeCO_3$) may precipitate.

$$MeCO_3(s) + CO_2(g) + H_2O \rightleftarrows Me^{+2} + 2HCO_3^-$$

This is dramatically supported by the presence of calcium and magnesium carbonates in the particulates. It is also supported by the high percent particulates for iron, nickel, calcium, magnesium and chromium in Table 2 and by the localization of these elements in particles. The very high percent particulates and high elemental masses for iron, nickel and calcium relative to other elements can only be explained by the precipitation of carbonates of these elements during filtration. About half or more of the iron, nickel and calcium were removed, presumably as crystals, during the filtration of waters CS-60, -62 and -63. Surface evaporation, presence in the oil fraction or bacterial removal cannot explain the high values. Crystals were not observed in water CS-60, presumably due to crystal decomposition prior to analysis as was verified for water CS-69.

Bacterial Removal

Bacterial cells that accumulate at the bottom of a sample container stored at >4°C may remove a significant fraction of the dissolved mercury, nickel and selenium and lesser amounts (<5%) of arsenic, bromine and iron. High concentrations of rod-shaped bacteria have been identified in the sediment that accumulates in retort waters stored at room temperature.[1] These bacteria have a surface charge and provide a high specific surface area which enhances adsorption. They may also remove elements by biological uptake. Table 4 indicates that large amounts of mercury and nickel are associated with the sediment material in all three samples studied and that lesser amounts of arsenic, bromine, iron, germanium and selenium are associated with the sediment of one or more of the samples. The most dramatic example of this behavior occurs for mercury. The samples in Table 2 with a high percent particulate loading for mercury (CS-60, -62, -63, -69, and -70) also have elevated percent particulate values for chromium, selenium and nickel relative to samples with low percent mercury particulate values. These elevated values cannot be explained by any of the previously discussed mechanisms and are likely due to association with the sediment material.

SUMMARY

Particulates were collected from 11 retort waters and their chemical composition and morphology studied using x-ray fluorescence spectrometry, x-ray diffraction and scanning electron microscopy. This work indicates that the particulate fraction of retort water consists of oils and tars, spent shale fines and bacterial cells. Crystals and finely dispersed salts may form during or after vacuum filtration and contribute to the particulate fraction. The crystal phase aragonite was positively identified in one sample. These particulates originate from the suspension of spent shale fines and the formation of an oil-water emulsion during retorting, from the evaporation of an equivalent 1-mm-deep layer of retort water from the filter surface, from CO_2 outgassing during filtration and from bacterial growth in samples maintained at >4°C.

The elements calcium, magnesium, iron, silicon, aluminum, potassium, sodium, nickel, barium, and chromium may be localized in individual particles and are major elements in the particulates. About one percent of the total potassium, arsenic, selenium, bromine, and rubidium in retort water is present in the particulate fraction and significantly greater than one percent of the iron, chromium, mercury and nickel. The elements arsenic, selenium, rubidium, strontium, mercury, gallium, lead, yttrium, titanium, and manganese are uniformly distributed in the matte material and occur at low levels. The elements mercury, nickel, germanium, arsenic, bromine, iron, and selenium appear to be removed by the bacterial cells.

ACKNOLWEDGEMENTS

Appreciation is extended to Robert Giauque and Lilly Goda of Lawrence Berkeley Laboratory for the x-ray fluorescence measurements, to Helena Reuben of Lawrence Berkeley Laboratory for the x-ray diffraction analyses, to Lucy Pacas of the Lawrence Berkeley Laboratory for the Zeeman atomic absorption spectroscopy measurements, and to Robert Heft of Lawrence Livermore Laboratory for the neutron activation analyses. This work was supported by the Division of Fossil Fuel Extraction of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

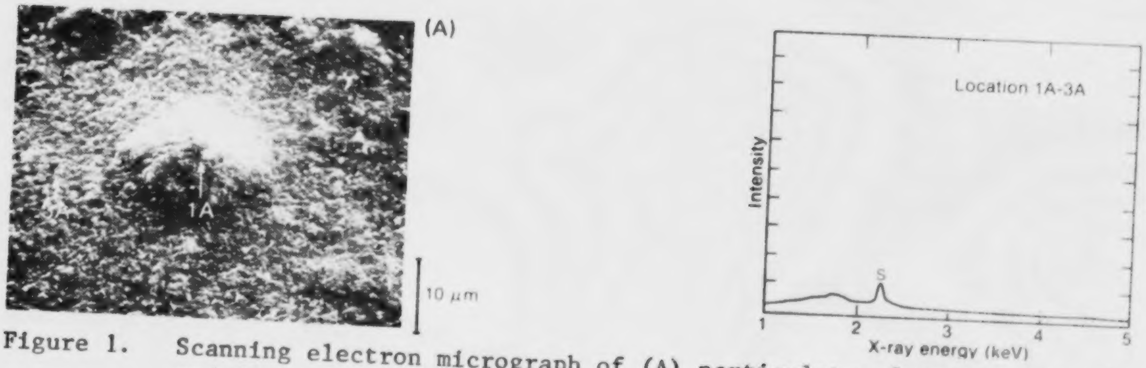

Figure 1. Scanning electron micrograph of (A) particulates from water CS-60 and diagrams of x-ray energy at locations 1A-3A. XBB 788-10560

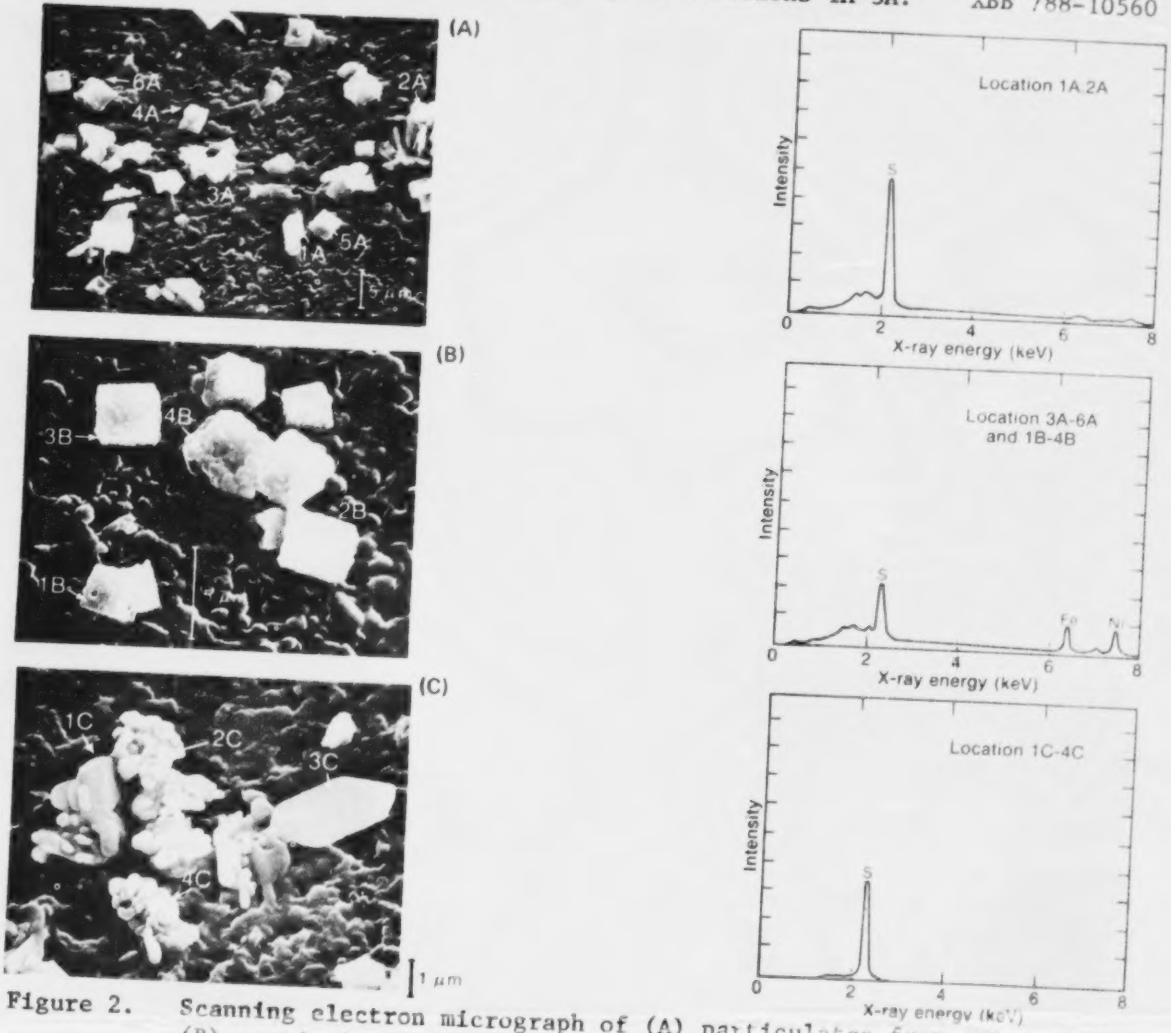

Figure 2. Scanning electron micrograph of (A) particulates from water CS-62; (B) particulates similar to those at locations 4A-6A in (A); (C) particulates from water CS-62; and diagrams of x-ray energy at locations 1A, 2A; 3A-6A and 1B-4B; and 1C-4C. XBB 788-10557, 58 and 59

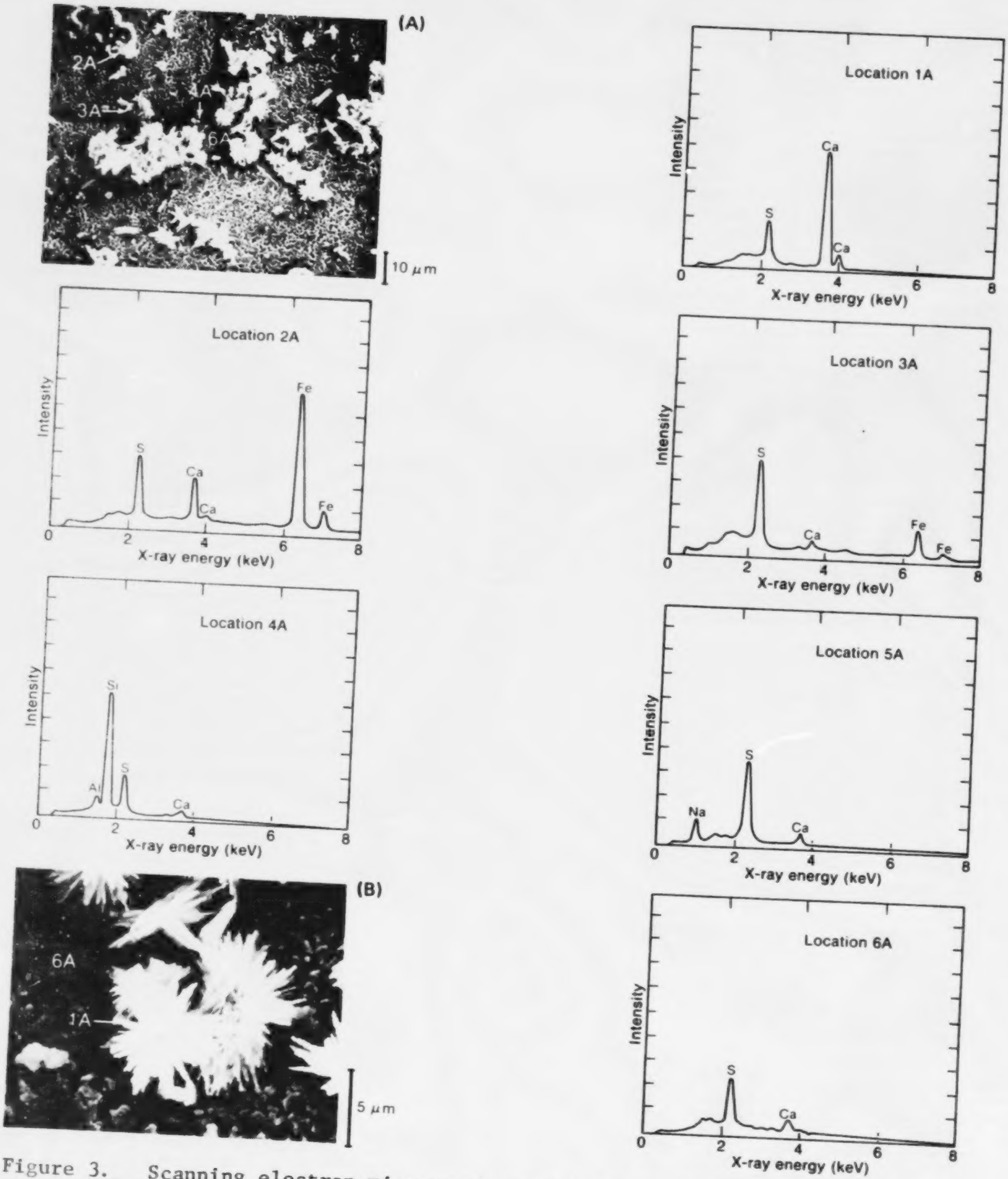

Figure 3. Scanning electron micrograph of (A) particulates from water CS-63; (B) detail of location 1A; and diagrams of x-ray energy at locations 1A; 2A; 3A; 4A; 5A; and 6A. XBB 788-10567 and 69

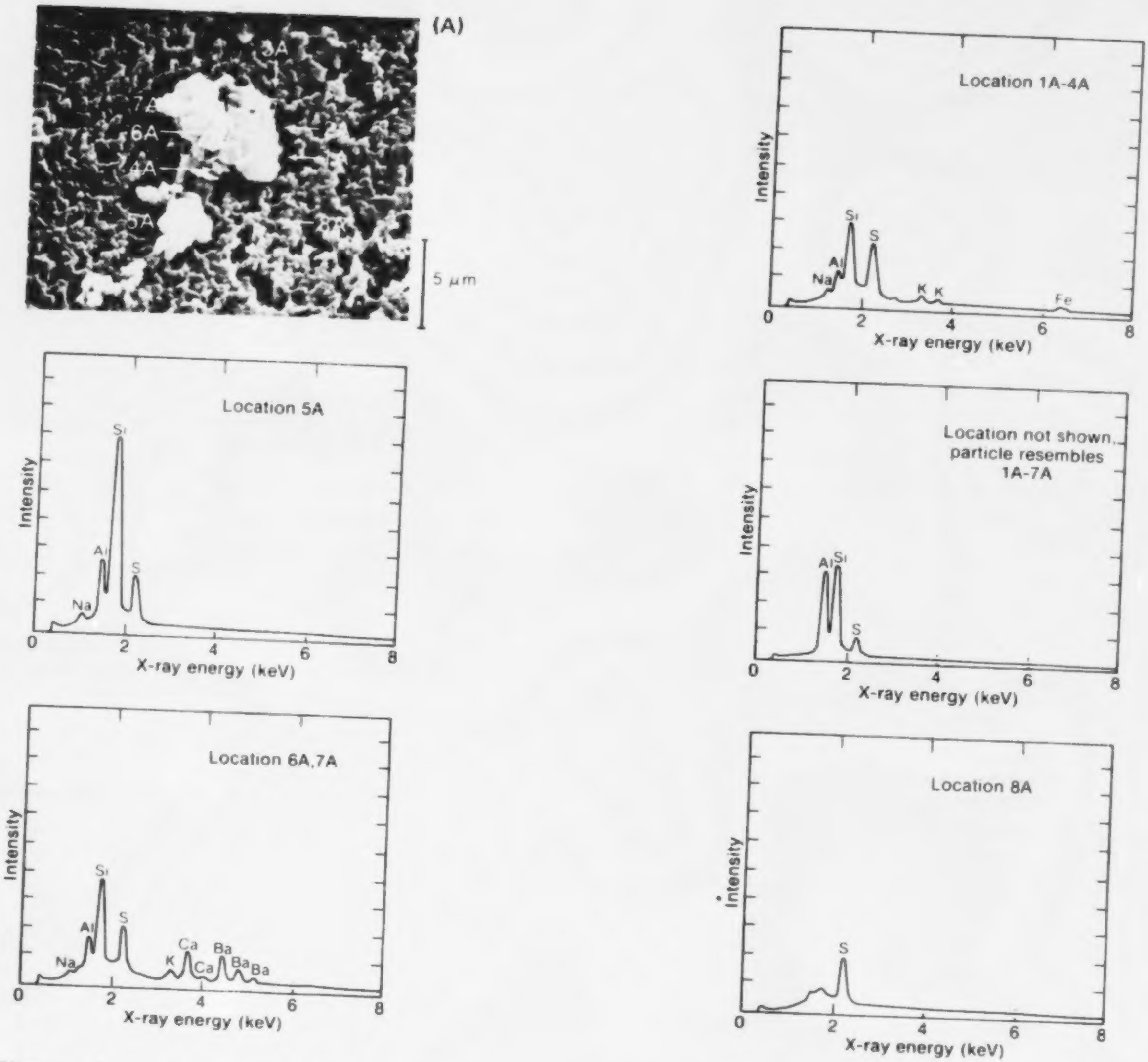

Figure 4. Scanning electron micrograph of (A) particulates from water CS-64; and diagrams of x-ray energy at locations 1A-4A; 5A; location resembling 1A-7A; 6A and 7A; and 8A.

XBB 788-10568

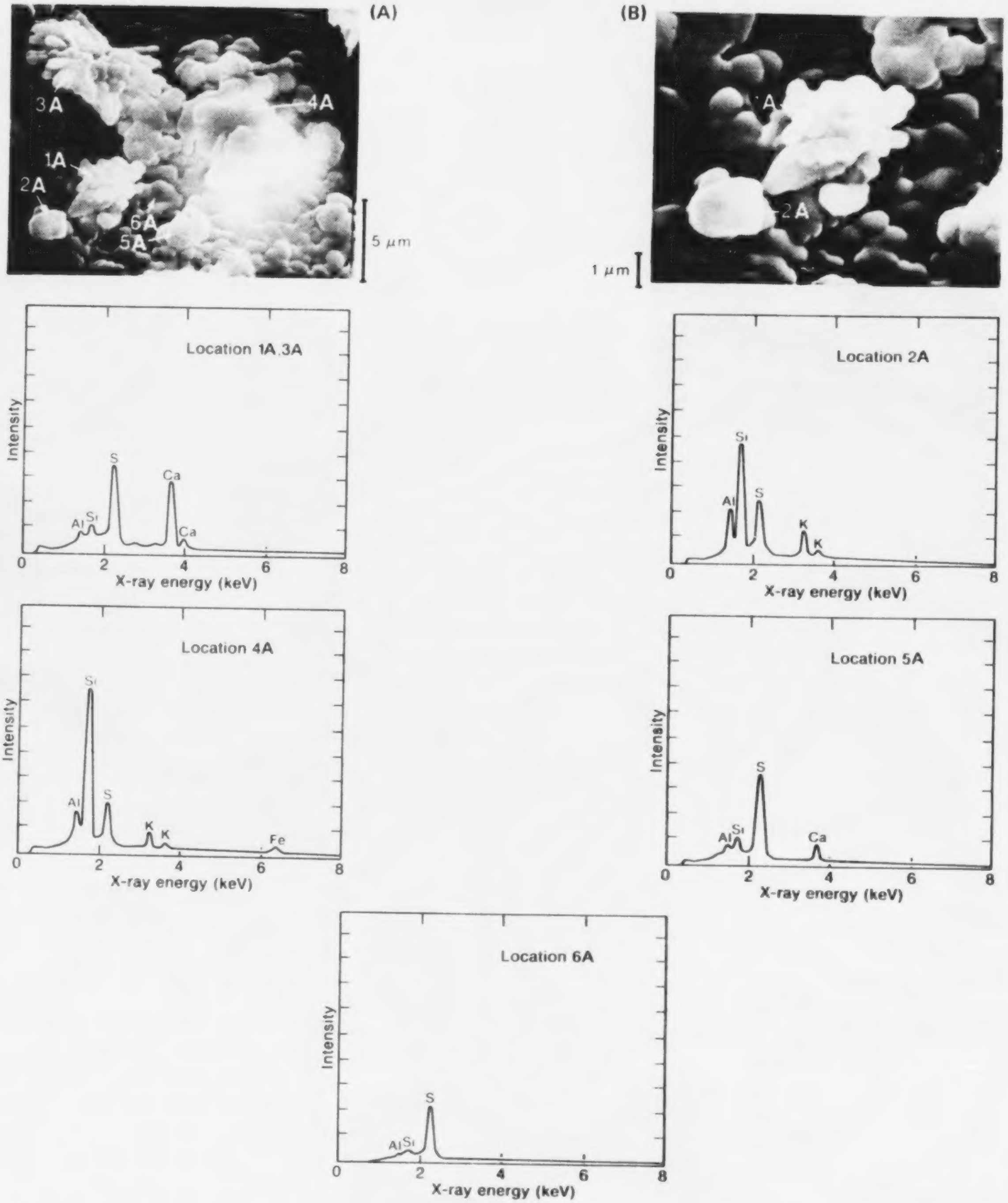

Figure 5. Scanning electron micrograph of (A) particulates from water CS-65; (B) detail of locations 1A,2A; and diagrams of x-ray energy at locations 1A, 3A; 2A; 4A; 5A; and 6A XBB 788-10572 and 74

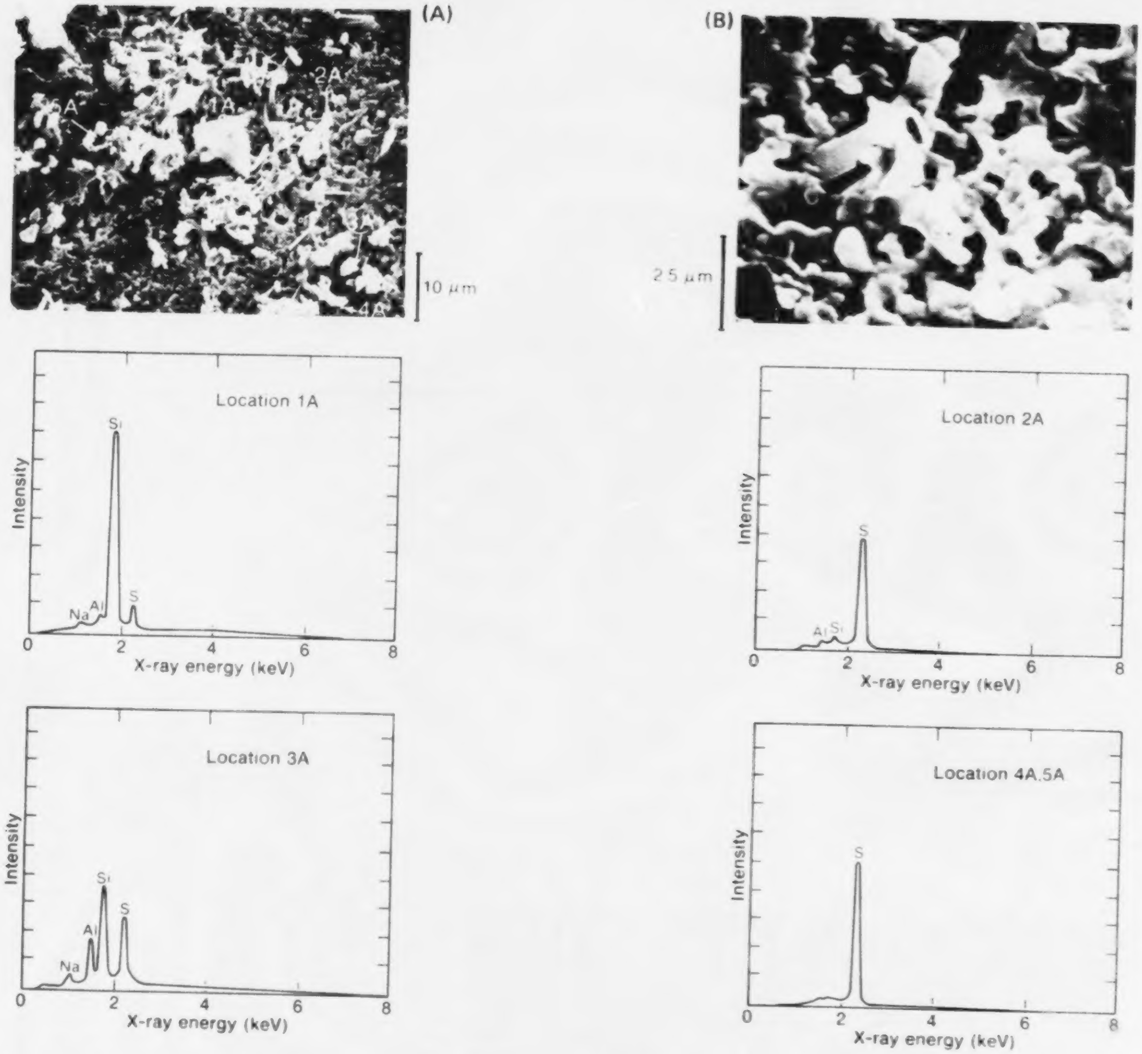

Figure 6. Scanning electron micrograph of (A) particulates from water CS-66; (B) detail of background in vicinity of location 1A; and diagrams of x-ray energy at locations 1A; 2A; 3A; and 4A, 5A.

XBB 788-10578 and 80

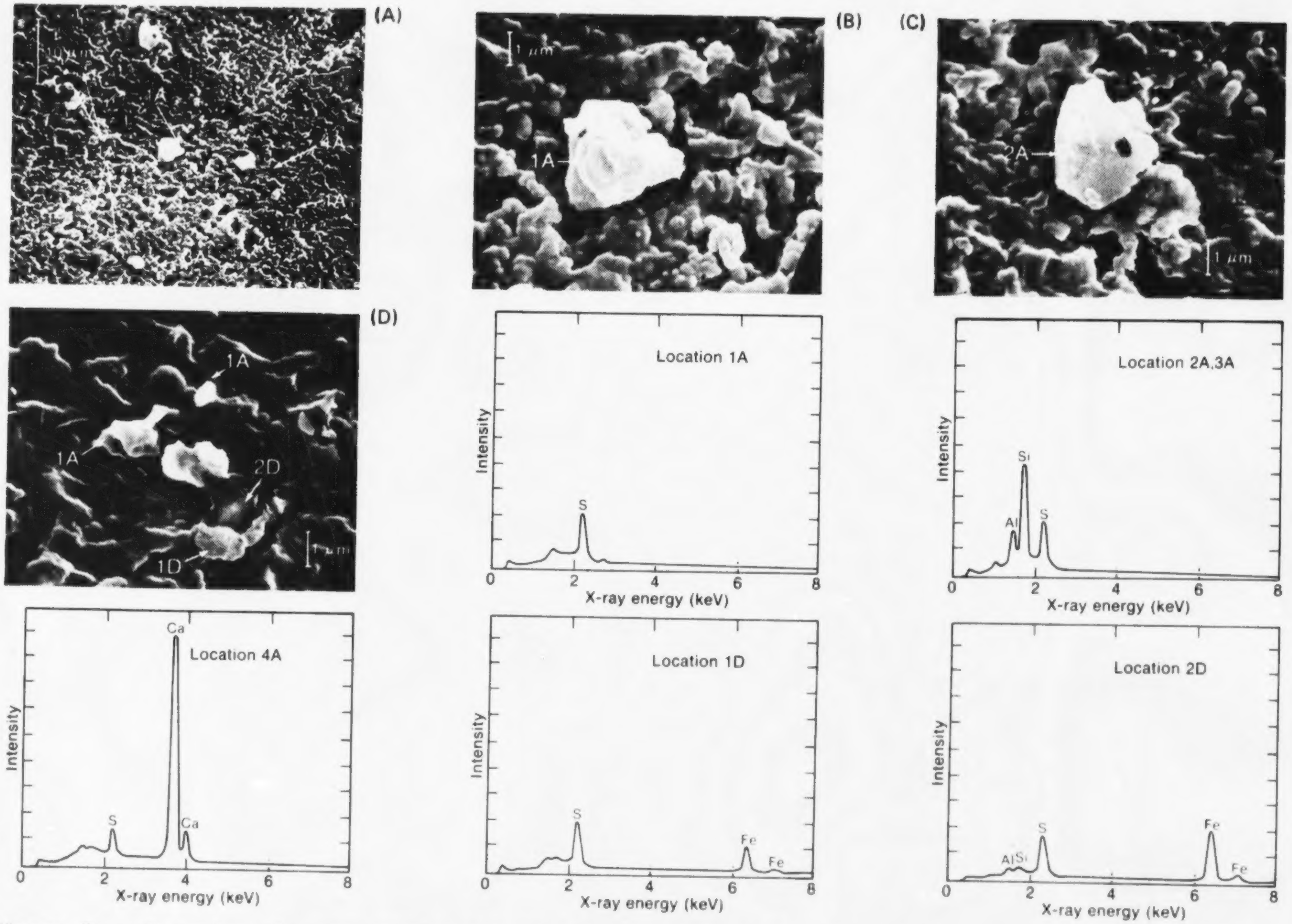

Figure 7. Scanning electron micrograph of (A) particulates from water CS-67; (B) detail of 1A at center field; (C) detail of 2A at top centers; (D) detail of upper left field; and diagrams of x-ray energy at locations 1A; 2A, 3A; 4A; 1D; and 2D.

XBB 788-10579, 76, 77, and 75

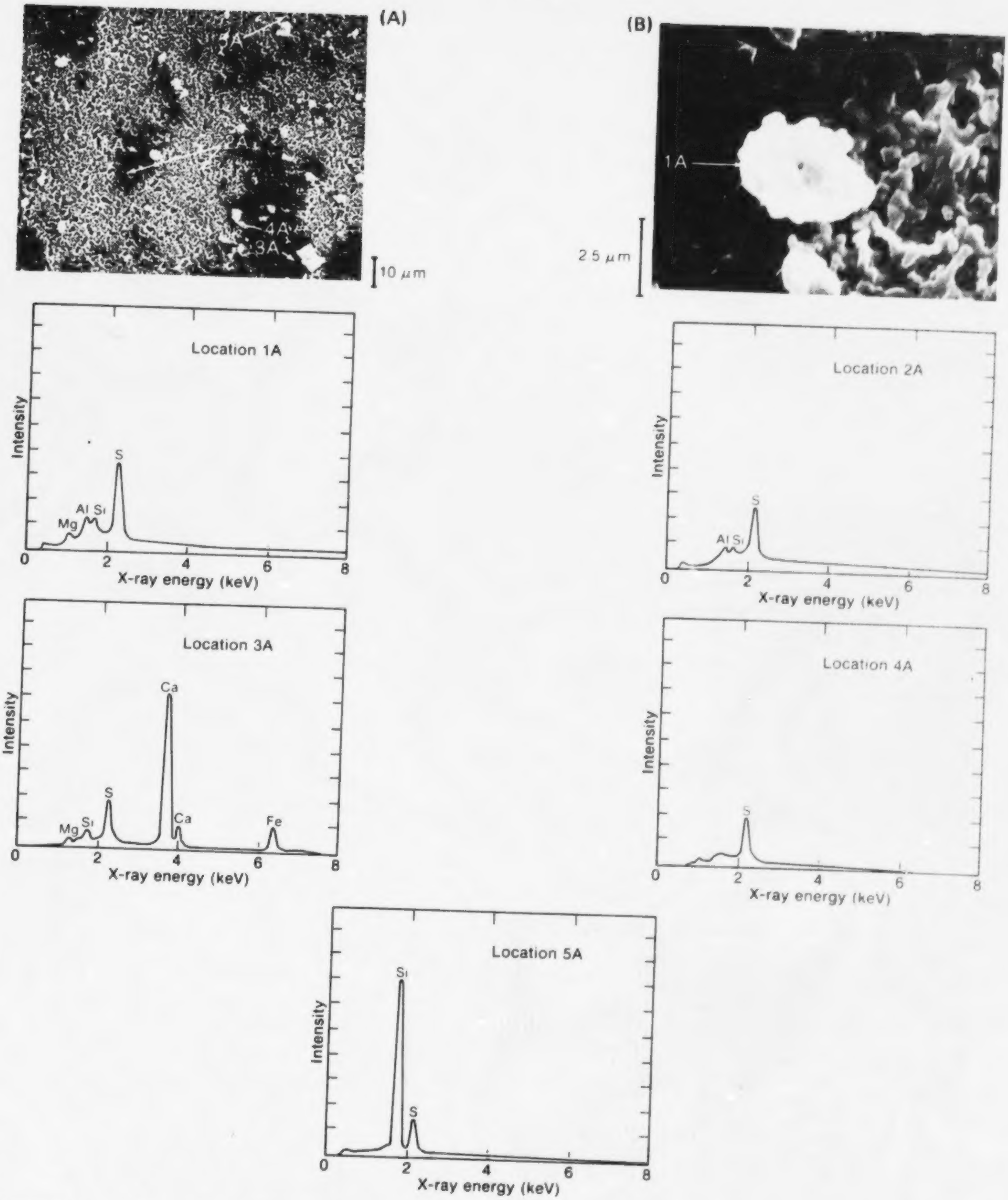

Figure 8. Scanning electron micrograph of (A) particulates from water CS-68; (B) detail of 1A; and diagrams of x-ray energy at locations 1A; 2A; 3A; 4A; 5A

XBB 788-10571 and 70

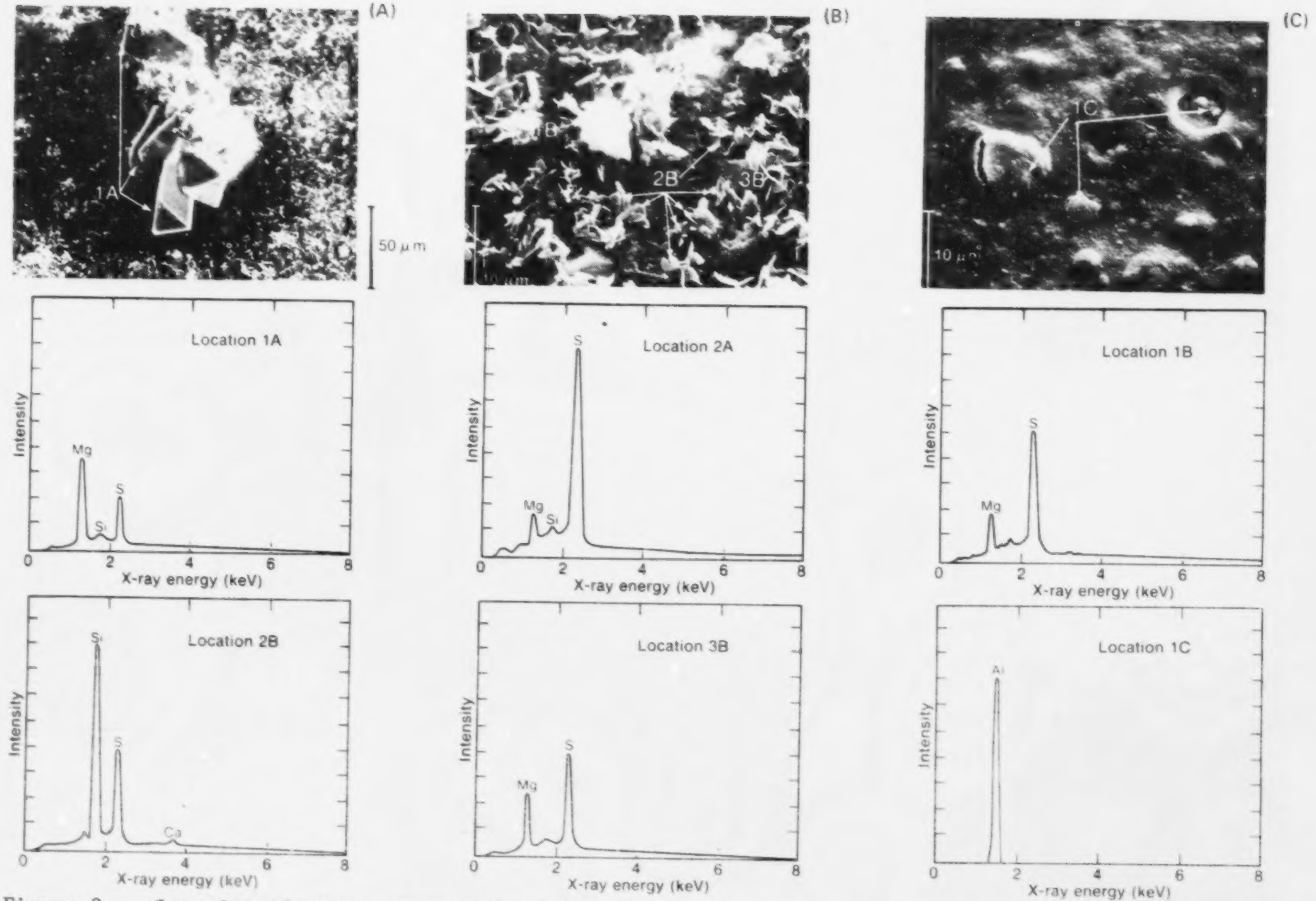

Figure 9. Scanning electron micrograph of (A) particulates from water CS-69; (B) more particulates from water CS-69; (C) particulates from water CS-69 one year after micrographs (A) and (B); and diagrams of x-ray energy at locations 1A; 2A; 1B, 2B; 3B; and 1C.

XBB 788-10565, 66 and XBB 795-6531

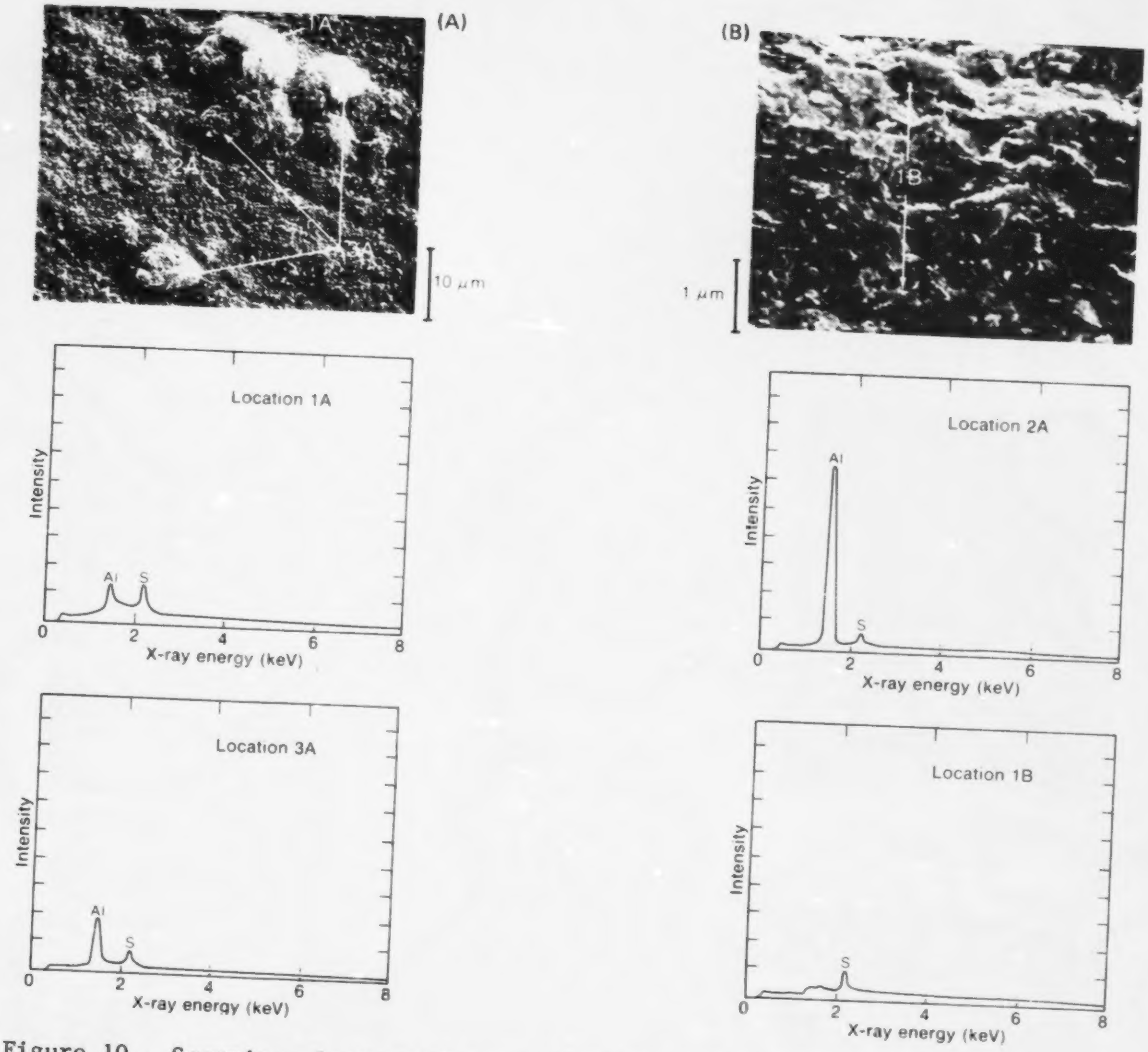

Figure 10. Scanning electron micrograph of (A) particulates from water CS-70; (B) more particulates from water CS-70; and diagrams of x-ray energy at locations 1A; 2A; 3A; and 1B. XBB 788-10563 and 62

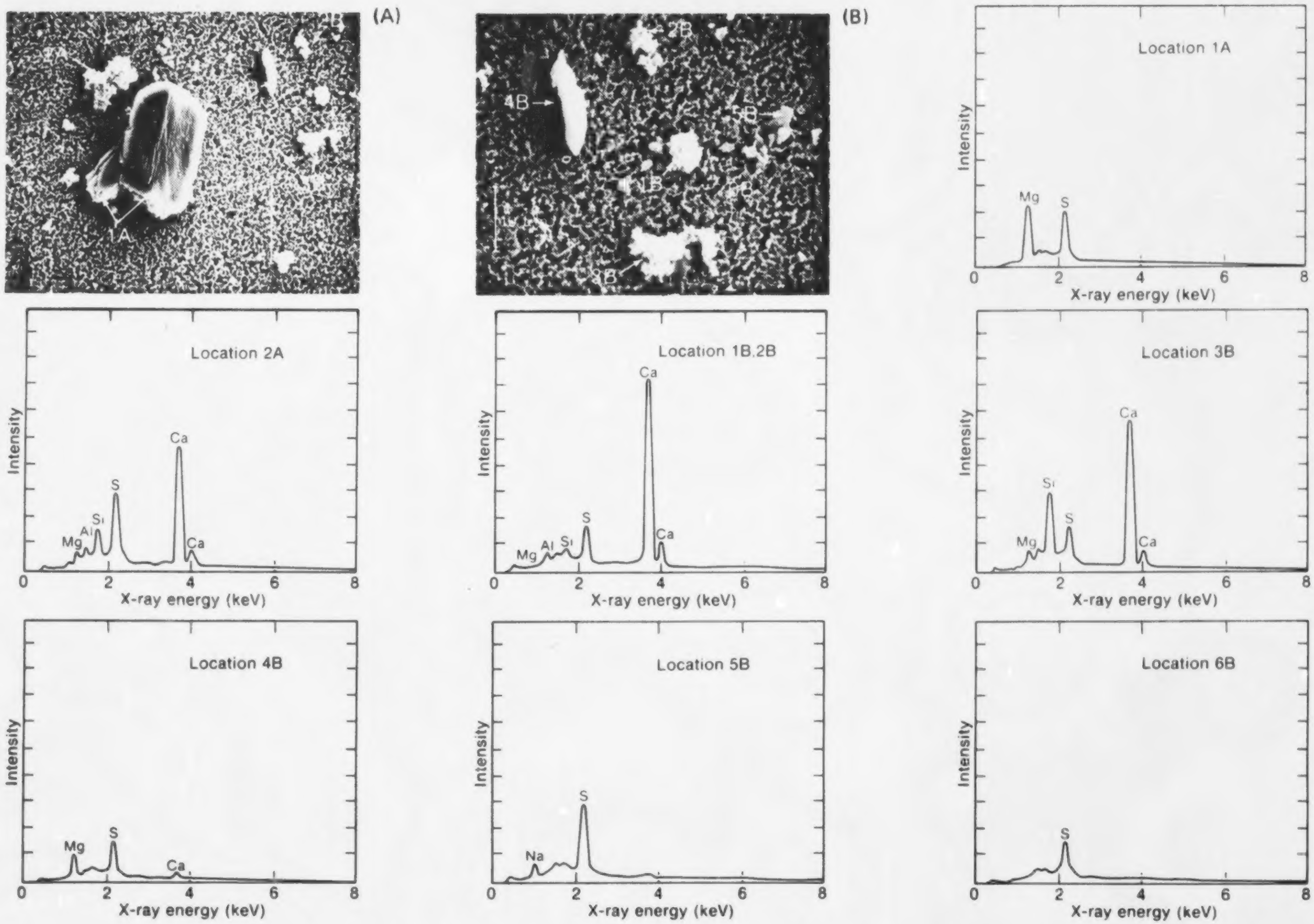

Figure 11. Scanning electron micrograph of (A) particulates from water CS-71; (B) detail of upper right field of (A); and diagrams of x-ray energy at locations 1A; 2A; 1B, 2B; 3B; 4B; 5B; and 6B.
XBB 788-10555 and 56

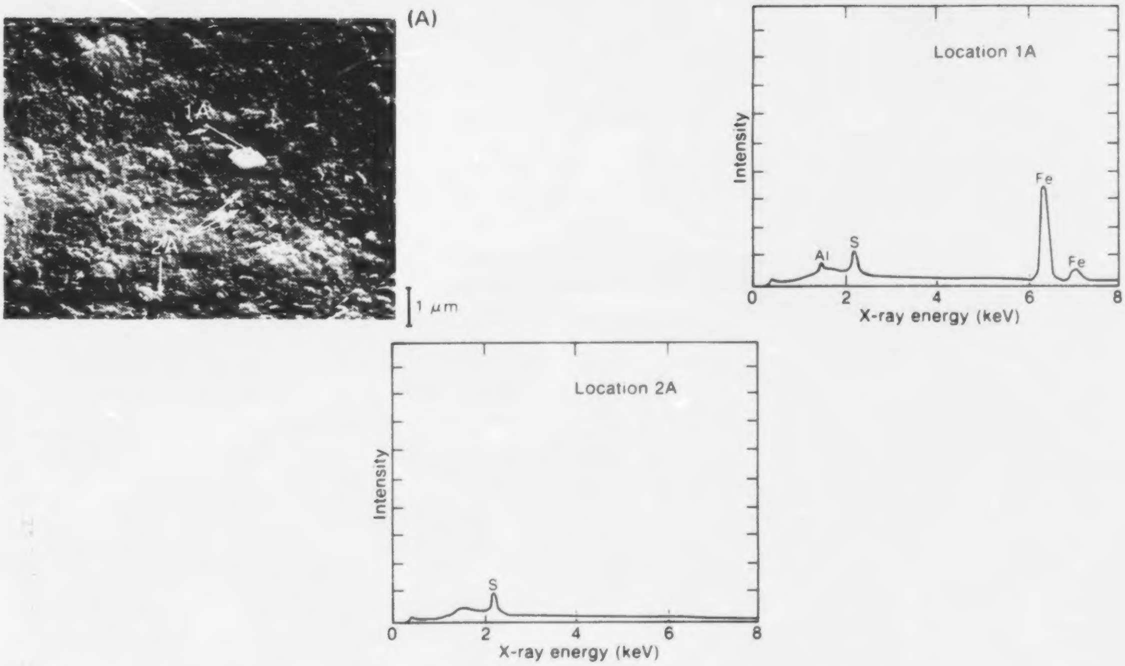

Figure 12. Scanning electron micrograph of (A) particulates from refiltered water CS-66F; and diagrams of x-ray energy at locations 1A; and 2A. XBB 788-10564

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ANALYSIS OF PARAHO OIL SHALE PRODUCTS AND EFFLUENTS: AN EXAMPLE OF THE MULTITECHNIQUE APPROACH

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INTRODUCTION

The source characterization studies detailed in this paper, which were sponsored by the U.S. Department of Energy, are intended to provide detailed and accurate information on the types and amounts of various substances which may be emitted to the environment from oil shale retorting processes, or which may find their way to the environment during subsequent portions of the shale oil cycle. Such information is of interest not only in its own right, but is also vital to related health and environmental fate and effect studies. The data presented here are related specifically to one process, the Paraho direct heated Semiworks Retort at Anvil Points, Colorado. However, it is probable that many of these data will have considerable general validity for all types of oil shale retorting processes.

The objectives of this initial characterization study were to: (1) obtain information on the partitioning of a number of trace and major elements of potential environmental significance into the various retort products and (2) obtain information on the physical and chemical forms of certain elements emitted from the retort. An additional important goal of the study was to find or develop and verify suitable analytical technology to meet these objectives.

DESCRIPTION OF THE PARAHO RETORT PROCESS

The Paraho surface retorting process has been described elsewhere (Jones 1976). It is presently operated by Development Engineering, Inc., (DEI) at Anvil Points, Colorado at the former U.S. Bureau of Mines site. The shale used in the process is obtained from a room and pillar mine in the Mahogany Zone of the Green River Formation. The mine at Anvil Points is located at about 2440 meters of elevation, some 600 meters above the present retort. At the processing site the mined shale is crushed and screened between minus 7.6 cm and plus 0.6 cm. The crushed shale fraction (10-15%) less than 0.6 cm is presently stockpiled.

DEI has recently operated two retorts at Anvil Points, an 0.77m ID by 18m high pilot plant unit and 2.6m ID by 23m semiworks retort. All of the studies detailed in this report were conducted on the semiworks retort.

Both of the retorts can be operated in either a direct or indirect heated mode. Since all of the samples used in this study were obtained during direct heat operation, this mode will be briefly described here.

In direct heated operation, illustrated in Figure 1, controlled combustion within the retort provides the heat necessary for retorting. The process is continuous and flows are countercurrent with the gas phase flowing upwards. The uniform downward flow of shale is controlled by a patented, hydraulically operated grate mechanism. Input raw shale is distributed evenly at the top by a rotating distributor and is then preheated by rising hot gases in the mist formation zone. Next, the preheated shale passes through the retorting zone where the organic "kerogen" is decomposed into an oil mist, gas and carbon residue (coke). The retorted shale then enters the combustion zone of the retort where the carbon residue and recycle gas serve as fuel for combustion. Input air is distributed evenly across the bed along with the recycle gas in this retort zone. In the bottom of the retort, the shale is cooled by the incoming bottom recycle gas, giving its heat to this gas; the retorted shale then exits through the bottom of the retort and is conveyed to a storage site. The oil mist produced is carried out the top of the retort through the offgas collector, and is separated from the gas by a coalescer and electrostatic precipitator. The product collected is an oil-water emulsion of about 5 wt % water. The emulsion produced during each shift is collected in a small gauging tank where it can be sampled. It is then pumped to a settling tank where the water is separated and drained, and "dry" product oil is then pumped to storage.

SAMPLE COLLECTION

Sampling is critical to a program of this type because meaningful analytical results are dependent on the integrity and representativeness of the samples. Obtaining representative samples from each important process stream at an operating pilot plant presents a number of difficulties. Contamination of the samples is another potential problem during field sampling operations. Fortunately, the Paraho Semiworks Retort is well designed for the purposes of sampling. After consultation with DEI personnel, a sampling program was developed to achieve the desired results. The samples were collected mainly during two field trips, one for four days in August 1977 and one for three days in November 1977. Sample collection and necessary onsite analyses were performed using a PNL camper-mounted mobile laboratory. The sample collection procedures have been described in detail elsewhere (Fruchter et al., 1979).

GENERAL SAMPLE PREPARATION

Solid Samples

Samples of the raw and retorted shale were received from the Paraho shale samplers as sand-sized particles or smaller. These samples were further ground to pass a 140-mesh sieve using alumina jar mills. Further grinding was considered unnecessary for analytical purposes because it had

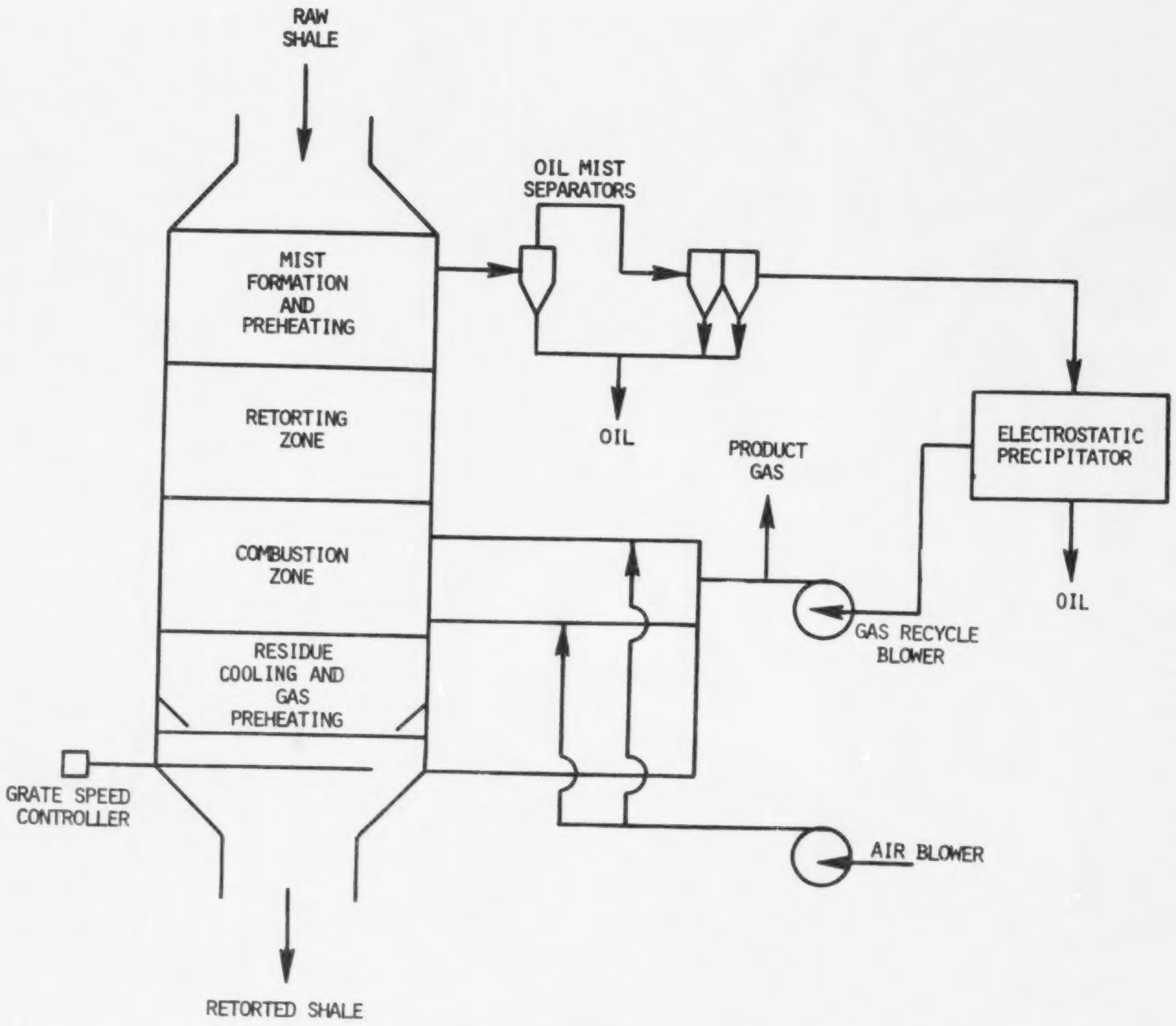

Figure 1. Paraho Surface Retorting Process (Direct Mode).

the potential for causing significant contamination and alteration of the samples. The samples were blended in a polyethylene mixer and split, using a riffle splitter, into 50-gram aliquots for analysis.

Liquid Samples

Oil samples were warmed to room temperature, shaken and sampled directly. They were not filtered.

The water samples were filtered at the plant site through quartz wool to remove oil and grease. No noticeable precipitate had formed in any samples except those that had been acidified. The acidified samples were further filtered at the laboratory. The other samples were shaken thoroughly and directly sampled. Further sample preparations for each analytical method are described elsewhere (Fruchter et al., 1979).

INORGANIC ANALYTICAL METHODS--THE MULTITECHNIQUE APPROACH

Many of the samples obtained from oil shale retorts are chemically and physically complex, creating the potential for matrix effects as well as other types of interferences in many of the commonly used methods for chemical analysis. Therefore, the techniques employed for inorganic analysis of the Paraho samples were chosen when possible for their relative freedom from matrix effects as well as their sensitivity and precision. Because no one method can at this time meet all of these requirements for all elements of interest, a multitechnique approach was adopted. This multitechnique approach to inorganic analysis also provided an opportunity to assess the strengths and weaknesses of the various methods for different samples. The major techniques used included instrumental neutron activation analysis, energy dispersive X-ray fluorescence analysis, D.C. arc plasma emission spectroscopy, flame atomic absorption spectroscopy and graphite furnace atomic adsorption spectroscopy, ion selective electrodes, hydride generation and various gas monitoring devices were used to supplement these techniques for specific elemental and speciation analysis.

ANALYSIS OF AUGUST 24, 1977 SAMPLES

Special attention was given to the analysis of samples collected on August 24, 1977, particularly the raw and retorted shale. There were several purposes behind this additional effort. First, a multitechnique intercomparison was carried out to enable objective assessment of the accuracy of the analytical data. The August 24 raw shale in particular was rigorously characterized for some 50 elements. A large quantity (15-20 kg) of this material has been archived and will eventually be made available to other workers in the field as an analytical reference material. The data given in this report combined with additional analyses provided by colleagues at Lawrence Berkeley Laboratory will form the basis for standardization of the material. In addition, a more limited analysis has been carried out on two lots to verify the homogeneity of the material.

Data Analysis

Tables 1 and 2 give the complete analytical results for analysis of the August 24, 1977 raw and retorted shale for 50 elements. In many cases several analytical techniques were used and it is possible to intercompare results. In general, six replicate samples were analyzed by each analytical technique. The analytical errors shown in Tables 1 and 2 are thus derived from the precision of six analyses. In a few cases only a single determination was made. These include the radiochemical measurement of Cd, Se, Zn, and U, the graphite furnace AA determination of Cd, and the cold-vapor AA determination of Hg. To reduce the data to a form suitable for graphical representation, a simple computer code, INCMP, was used. INCMP performs the following operations:

1. A minimum error of 2% is assigned to all data. Any data with a reported error less than 2% is set equal to 2%.
2. An error weighted average of the data is computed for each element.
3. If more than two analyses are reported, Chauvenet's criterion is then applied and, if necessary, the worst outlier rejected. A new error weighted average is then computed. This procedure was only followed once due to the small size of each data set. Very few determinations were actually rejected in this manner. Those which were rejected are noted with an asterisk in Tables 1 and 2.
4. Once an appropriate average value has been determined, a percentage deviation of each individual value from the mean for that element is computed. These values together with the appropriate percentage standard deviation for each point in the raw shale sample are plotted in Figure 2. This format is convenient for viewing all of the data at once. Only elements which were analyzed by more than one reliable technique are plotted; individual determinations rejected by Chauvenet's criterion (step 3) are omitted.
5. Additionally, a percent root mean squared deviation is computed for each group of data (shown at top of Figure 2) and a chi squared test was applied to test the validity of the error analysis.

A number of observations can be drawn from Figure 2. Agreement between analytical methods is in general quite good, and in almost all cases the error bars overlap. One notable exception is the determination of As in the raw shale by instrumental neutron activation and X-ray fluorescence. This difference is only noticeable since both methods have good precision. Even in this case the disagreement is only 10-15%. A wide range of precision is evident, illustrating the advantages of using several different analytical techniques for multielement analysis.

TABLE 1. MULTIELEMENT ANALYSIS OF PARAHO-FEEDSTOCK SHALE COLLECTED 8/24/77
(in ppm except as noted)

Element	INAA	RCAA	XRF	PES	FAA	GFAA	CVAA	Error Weighted Average
Al (%)	3.89 ± 1.4			3.78 ± 0.08	3.69 ± 0.11			3.77 ± 0.06
As	48.0 ± 0.7		41.6 ± 5.0					44.3 ± 0.6
B				94.0 ± 2.0				94.0 ± 2.0
Ba	483.0 ± 34.0			515.0 ± 8.0				512.0 ± 10.0
Br	0.57 ± 0.13							0.57 ± 0.13
Ca (%)	10.4 ± 0.5		10.7 ± 0.5	9.9 ± 0.1	11.0 ± 0.4*			10.1 ± 0.2
Cd		0.64 ± 0.03				0.61 ± 0.08		0.64 ± 0.03
Ce	43.1 ± 0.9							43.1 ± 0.9
Co	9.0 ± 0.1							9.0 ± 0.1
Cr	36.7 ± 1.8		39.7 ± 9.3	33.8 ± 0.6				34.2 ± 0.6
Cs	3.84 ± 0.22							3.84 ± 0.22
Cu			40.3 ± 2.3	40.0 ± 5.5				40.3 ± 2.1
Dy	2.4 ± 0.4							2.4 ± 0.4
Eu	0.60 ± 0.02							0.60 ± 0.02
Fe (%)	2.08 ± 0.04		2.02 ± 0.10	2.01 ± 0.04	2.14 ± 0.04			2.07 ± 0.02
Ga			8.4 ± 0.8					1.75 ± 0.05
Hf	1.75 ± 0.05							1.75 ± 0.05
Hg							0.089 ± 0.005	0.089 ± 0.005
Ho	0.67 ± 0.11							0.67 ± 0.11
K (%)	1.69 ± 0.11		1.66 ± 0.02	1.79 ± 0.03	1.55 ± 0.03			1.61 ± 0.02
La	20.6 ± 0.7							20.6 ± 0.7
Lu	0.28 ± 0.03							0.28 ± 0.03
Mg (%)				3.42 ± 0.05	3.59 ± 0.3			3.46 ± 0.06
Mn	312.0 ± 20.0		319.0 ± 20.0	314.0 ± 22.0				315.0 ± 12.0
Mo			24.0 ± 2.5	20.9 ± 1.9				22.0 ± 1.5
Na (%)	1.68 ± 0.01				1.73 ± 0.07			1.69 ± 0.03
Nb			8.0 ± 0.7					8.0 ± 0.7
Nd	20.4 ± 2.1							20.4 ± 2.1
Ni	23.0 ± 5.3		24.2 ± 1.2	27.6 ± 0.6				27.5 ± 0.6
Pb			26.5 ± 2.1					26.5 ± 2.1
Rb	74.9 ± 2.3		74.0 ± 2.7					74.5 ± 1.8
S			5730.0 ± 500					5730.0 ± 500.0
Sb	2.09 ± 0.08							2.09 ± 0.08
Sc	5.77 ± 0.16							5.77 ± 1.6
Se	2.1 ± 0.2	2.0 ± 0.1	2.7 ± 0.7					2.03 ± 0.09
Si (%)			14.1 ± 0.7		15.2 ± 0.1			15.0 ± 0.3
Sm	3.10 ± 0.3							3.10 ± 0.3
Sr	674.0 ± 24.0		678.0 ± 21.0	712.0 ± 14.0				696.0 ± 11.0
Ta	0.55 ± 0.02							0.55 ± 0.02
Tb	0.37 ± 0.03							0.37 ± 0.03

TABLE 1. MULTIELEMENT ANALYSIS OF PARAHO-FEEDSTOCK SHALE COLLECTED 8/24/77 (CONTINUED)
(in ppm except as noted)

Element	INAA	RCAA	XRF	PES	FAA	GFAA	CVAA	Error Weighted Average
Th	6.33 ± 0.13							6.33 ± 0.13
Ti	0.18 ± 0.02		0.17 ± 0.02		0.18 ± 0.01			0.18 ± 0.01
U	4.2 ± 0.3	4.6 ± 0.2						4.5 ± 0.2
V	86.0 ± 6.0		95.0 ± 6.0	96.0 ± 3.0				94.2 ± 2.4
Y			14.0 ± 1.0					14.0 ± 1.0
Yb	1.26 ± 0.11							1.26 ± 0.11
Zn	67.2 ± 3.7	63.0 ± 3.0	62.6 ± 2.3	73.2 ± 4.0*				63.6 ± 1.6
Zr				36.2 ± 1.3				36.2 ± 1.3

*Deleted from error weighted average.

INAA - Instrumental Neutron Activation Analysis
RCAA - Radiochemical Neutron Activation Analysis
XRF - X-Ray Fluorescence Analysis

PES - Plasma Emission Spectroscopy (Sodium Carbonate Fusion)
FAA - Conventional Flame Atomic Absorbtion (Lithium Metaborate Fusion)
GFAA - Graphite Furnace Atomic Absorbtion
CVAA - Cold Vapor Atomic Absorbtion

TABLE 2. MULTIELEMENT ANALYSIS OF PARAHO RETORTED SHALE COLLECTED 8/24/77
(in ppm except as noted)

Element	INAA	RCAA	XRF	PES	FAA	GFAA	CVAA	Error Weighted Average
Al (%)	4.83 ± 0.05			4.46 ± 0.05	4.56 ± 0.17			4.83 ± 0.10
As	59.2 ± 0.9		59.8 ± 1.9					59.4 ± 1.0
B				107.0 ± 2.0				107.0 ± 2.0
Ba	593.0 ± 13.0			613.0 ± 12.0				604.0 ± 9.0
Br	0.80 ± 0.18							0.80 ± 0.18
Ca (%)	13.1 ± 0.5		13.9 ± 0.7	11.1 ± 0.2	13.2 ± 0.2			13.3 ± 0.2
Cd		0.90 ± 0.04				0.99 ± 0.13		0.91 ± 0.04
Ce	51.5 ± 1.5							51.5 ± 1.5
Co	11.1 ± 0.2							11.1 ± 0.2
Cr	44.3 ± 0.9		49.6 ± 8.9	41.0 ± 3.8				44.2 ± 0.9
Cs	4.68 ± 0.21							4.68 ± 0.21
Cu			56.3 ± 1.0	46.9 ± 5.3				55.9 ± 1.1
Dy	3.5 ± 0.2							2.4 ± 0.4
Eu	0.73 ± 0.02							0.73 ± 0.02
Fe (%)	2.42 ± 0.04		2.56 ± 0.13	2.35 ± 0.03	2.47 ± 0.08			2.40 ± 0.030
Ga			11.6 ± 1.2					11.6 ± 1.2
Hf	2.11 ± 0.03							2.11 ± 0.03
Hg							0.035 ± 0.003	0.035 ± 0.003
Ho	0.88 ± 0.04							0.88 ± 0.04
K (%)	1.98 ± 0.20		1.94 ± 0.05	2.11 ± 0.05*	1.81 ± 0.03			1.86 ± 0.03
La	24.7 ± 0.3							24.7 ± 0.3
Lu	0.35 ± 0.03							0.35 ± 0.03
Mg (%)				3.88 ± 0.03	4.32 ± 0.09			4.07 ± 0.06
Mn	388.0 ± 23.0		420.0 ± 24.0	374.0 ± 28.0				396.0 ± 14.0
Mo			32.7 ± 1.4	41.3 ± 3.9				33.7 ± 1.3
Na (%)	2.15 ± 0.03				2.24 ± 0.03			2.19 ± 0.03
Nb			9.2 ± 1.5					9.2 ± 1.5
Nd	22.3 ± 1.1							22.3 ± 1.1
Ni	29.7 ± 4.6		32.1 ± 3.9	32.4 ± 1.8				
Pb			36.2 ± 2.0					36.2 ± 2.0
Rb	89.9 ± 4.1		88.0 ± 2.0					88.4 ± 1.8
S			6780.0 ± 620.0					6780.0 ± 620.0
Sb	2.63 ± 0.15							2.63 ± 1.5
Sc	6.84 ± 0.15							6.84 ± 0.15
Se		2.3 ± 0.1	3.4 ± 0.5					2.3 ± 0.1
Si (%)			17.8 ± 1.3		18.2 ± 0.3			18.2 ± 0.4
Sm	3.68 ± 0.07							3.68 ± 0.07
Sr	820.0 ± 26.0*		866.0 ± 7.0	892.0 ± 14.0				879.0 ± 12.0
Ta	0.65 ± 0.02							0.65 ± 0.02
Tb	0.42 ± 0.04							0.42 ± 0.04

TABLE 2. MULTIELEMENT ANALYSIS OF PARAHO RETORTED SHALE COLLECTED 8/24/77 (CONTINUED)
(in ppm except as noted)

Element	INAA	RCAA	XRF	PES	FAA	GFAA	CVAA	Error Weighted Average
Th	7.35 ± 0.10							7.55 ± 0.10
Ti	0.21 ± 0.04		0.24 ± 0.01		0.20 ± 0.03			0.24 ± 0.01
U	5.3 ± 0.2	4.9 ± 0.2						5.10 ± 0.14
V	111.0 ± 13.0		139.0 ± 19.0	133.0 ± 7.0				129.0 ± 6.0
Y			16.4 ± 0.9					16.4 ± 0.9
Yb	1.61 ± 0.13							1.61 ± 0.13
Zn	89.2 ± 3.0	77.0 ± 4.0	86.2 ± 5 5	93.6 ± 5.3				82.3 ± 2.2
Zr			61.5 ± 2.8	36.2 ± 1.3				36.2 ± 1.3

*Deleted from error weighted average.

INAA - Instrumental Neutron Activation Analysis
RCAA - Radiochemical Neutron Activation Analysis
XRF - X-Ray Fluorescence Analysis

PES - Plasma Emission Spectroscopy (Sodium Carbonate Fusion)
FAA - Conventional Flame Atomic Absorbtion (Lithium Metaborate Fusion)
GFAA - Graphite Furnace Atomic Absorbtion
CVAA - Cold Vapor Atomic Absorbtion

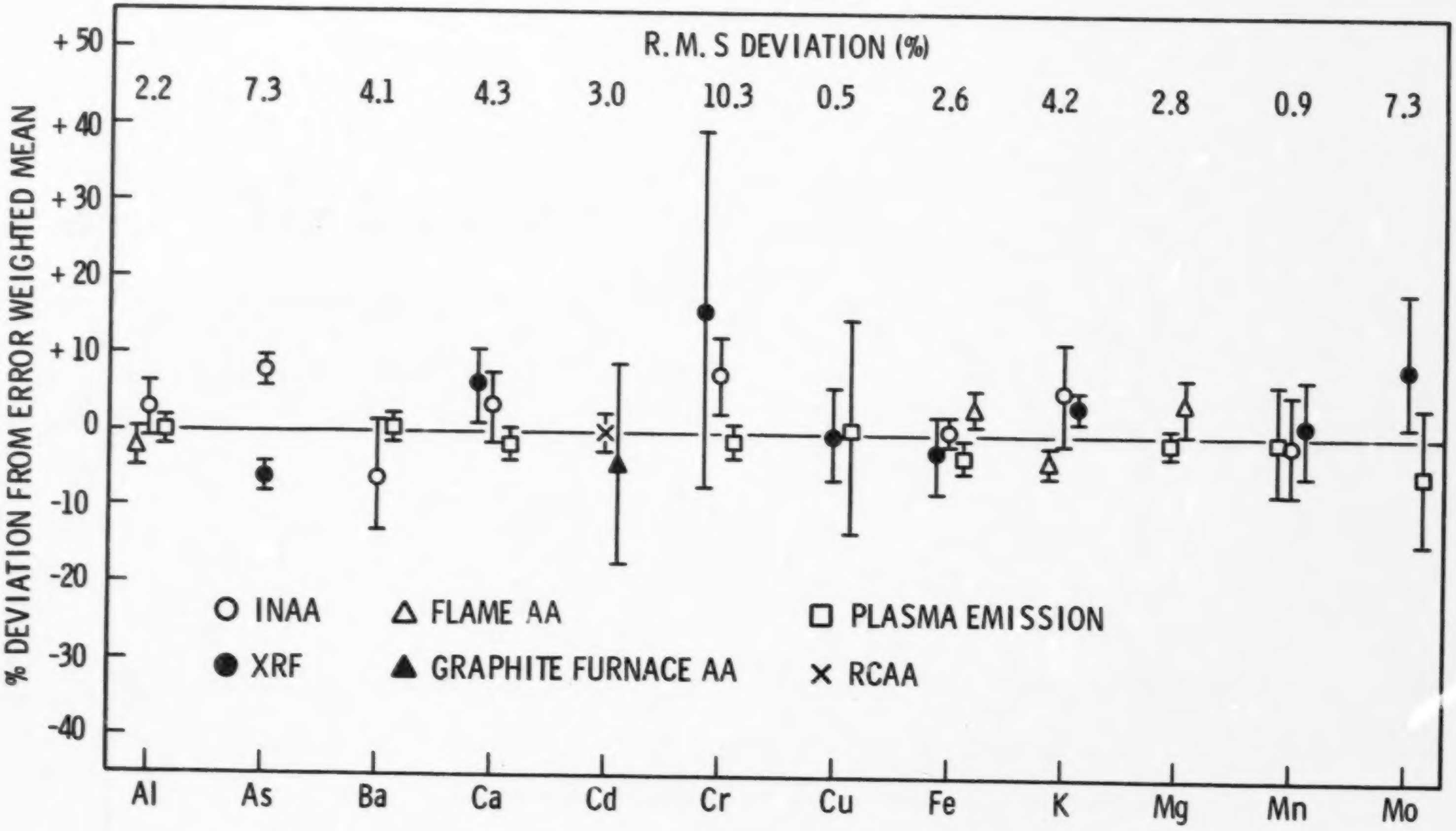

Figure 2. Relative Performance of Analytical Techniques Used in the Multielement Analysis of Paraho Raw Oil Shale (8-24-77).

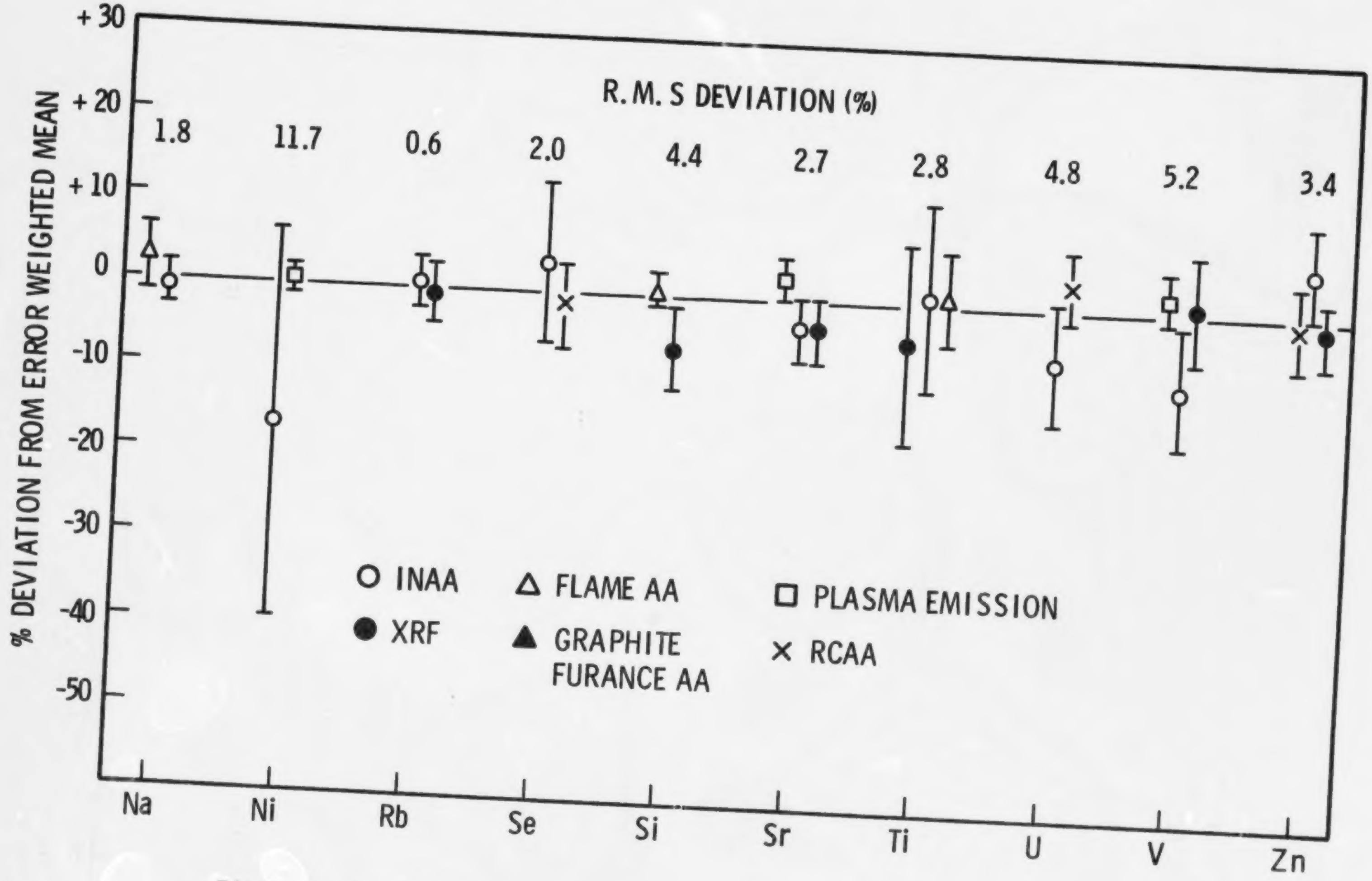

Figure 2. (Cont.) Relative Performance of Analytical Techniques Used in the Multielement Analysis of Paraho Raw Oil Shale (8-24-77).

Retorted/Raw Element Ratios

The ratio of an element in the retorted shale to the same element in raw shale is useful for assessing a material balance. Furthermore, any systematic analytical errors should tend to cancel when a ratio is computed. To test that premise, the ratio was calculated in a number of different ways. Table 3 shows the elemental ratios calculated from the data in Tables 1 and 2 with error propagated quadratically. An error weighted average of the data for each element is given in the last column of Table 3. Table 4 provides a summary of the average ratio calculated for each technique with suspected volatile elements such as As, Cd, Se, S and Hg deliberately omitted. An overall unweighted average was computed for the best data on approximately 20 nonvolatile elements yielding a ratio of 1.20 ± 0.02. The loss of raw shale mass expected simply from the Fischer assay should yield mineral phase element enrichments of only about 1.10 in the retorted shale. The additional 10% enrichment observed for the Paraho combustive retorting process is evidently due to unaccounted water and gas losses and to CO_2 loss through thermal decomposition of dolomite and calcite.

The dashed lines shown in Figure 3 show the limits of the average ratio computed above (1.20 ± 0.02). Mercury is clearly being released and redistributed into products other than the retorted shale. At the maximum retorting temperature (~600°C), the mercury should be quantitatively removed. The mercury found on the retorted shale has probably been recondensed from the recycle gas. Sulfur is presumably also lost; however, that is not determinable from the XRF analysis due to poor precision. Cadmium actually seems to show a small additional enrichment in the retorted shale. Cadmium has been shown to be mobilized somewhat during _in situ_ retorting (Fox et al., 1977). Graphite furnace atomic absorption studies in our laboratory on raw and retorted shale show volatilization of cadmium at 500-600°C, in the same range as the maximum temperature reached in the Paraho process. Some of the cadmium may thus be redistributed by the recycle gas during retort operations. Temperature fluctuation during retort operation may account for a nonequilibrium excell. Clearly more work is needed on cadmium because its behavior is very sensitive to retorting conditions.

REDISTRIBUTION OF ELEMENTS AMONG THE PRODUCTS

The redistribution of elements from the raw shale to the products and effluents was calculated from the data in Tables 1 and 2 and from analyses for oil, water and gas presented in Tables 5, 6 and 7. Tables 5, 6 and 7 also show the amount of redistribution to each phase. The total redistribution can be characterized into three categories. The first category (I) includes the elements which remain almost totally with the retorted shale and have partitioning coefficients of less than 0.01% for the product oil, product water, and product gas. This group includes the elements Al, Ba, Ca, Cr, K, Mg, Mn, Na, Rb, Si, and Sr. The second category is characterized by elements which have a cumulative partitioning coefficient (products other than retorted shale) of from 0.01 to approximately 5%. This second category (II) includes the elements As, B, Co, Cu, Fe, Ni, Sb, Se, Fe, Th, Ti, V, and

TABLE 3. RATIO OF ELEMENT IN RETORTED SHALE TO ELEMENT IN RAW SHALE

Element	INAA	RCAA	XRF	PES	FAA	GFAA	CVAA	Error Weighted Average
Al	1.24 ± 0.05			1.18 ± 0.03	1.24 ± 0.06			1.24 ± 0.024
As	1.23 ± 0.03		1.44 ± 0.05					1.29 ± 0.03
B				1.14 ± 0.03				1.14 ± 0.03
Ba	1.23 ± 0.09			1.19 ± 0.03				1.19 ± 0.03
Br	1.40 ± 0.45							1.40 ± 0.45
Ca	1.26 ± 0.08		1.30 ± 0.09	1.12 ± 0.02*	1.20 ± 0.05			1.23 ± 0.04
Cd		1.41 ± 0.09				1.62 ± 0.30		1.43 ± 0.09
Ce	1.20 ± 0.04							1.20 ± 0.04
Co	1.23 ± 0.03							1.23 ± 0.03
Cr	1.21 ± 0.02		1.21 ± 0.06	1.21 ± 0.11				1.21 ± 0.03
Cs	1.22 ± 0.09							1.22 ± 0.09
Cu			1.40 ± 0.08	1.17 ± 0.21				1.37 ± 0.08
Dy	1.45 ± 0.26							1.45 ± 0.26
Eu	1.22 ± 0.05							1.22 ± 0.05
Fe (%)	1.16 ± 0.03		1.27 ± 0.09	1.17 ± 0.03	1.15 ± 0.04			1.17 ± 0.02
Ga			1.38 ± 0.19					1.38 ± 0.19
Hf	1.21 ± 0.04							1.21 ± 0.04
Hg								0.39 ± 0.04
Ho	1.31 ± 0.22							1.31 ± 0.22
K (%)	1.17 ± 0.15		1.17 ± 0.03	1.18 ± 0.03	1.17 ± 0.03			1.17 ± 0.02
La	1.20 ± 0.02							1.20 ± 0.02
Lu	1.25 ± 0.17							1.25 ± 0.17
Mg (%)				1.13 ± 0.02	1.20 ± 0.05			1.14 ± 0.02
Mn	1.24 ± 0.11		1.32 ± 0.11	1.19 ± 0.12				1.24 ± 0.07
Mo			1.36 ± 0.15	1.98 ± 0.26*				1.33 ± 0.15
Na	1.28 ± 0.02				1.29 ± 0.06			1.28 ± 0.02
Nb			1.15 ± 0.21					1.15 ± 0.21
Nd	1.09 ± 0.12							1.09 ± 0.12
Ni	1.29 ± 0.36		1.33 ± 0.17	1.17 ± 0.07				1.20 ± 0.06
Pb			1.37 ± 0.13					1.37 ± 0.13
Rb	1.20 ± 0.07		1.19 ± 0.05					1.19 ± 0.04
S			1.18 ± 0.15					1.18 ± 0.15
Sb	1.26 ± 0.09							1.26 ± 0.09
Sc	1.19 ± 0.04							1.19 ± 0.04
Se		1.15 ± 0.08	1.26 ± 0.37					1.16 ± 0.08
Si			1.26 ± 0.04		1.20 ± 0.02			1.20 ± 0.02
Sm	1.19 ± 0.03							1.19 ± 0.03
Sr	1.22 ± 0.06		1.28 ± 0.04	1.25 ± 0.03				1.26 ± 0.02
Ta	1.18 ± 0.06							1.18 ± 0.06
Tb	1.14 ± 0.14							1.14 ± 0.14

TABLE 3. RATIO OF ELEMENT IN RETORTED SHALE TO ELEMENT IN RAW SHALE (CONTINUED)

Element	INAA	RCAA	XRF	PES	FAA	GFAA	CVAA	Error Weighted Average
Th	1.19 ± 0.03							1.19 ± 0.03
Ti	1.17 ± 0.26		1.41 ± 0.18		1.11 ± 0.17			1.33 ± 0.15
U	1.26 ± 0.10	1.07 ± 0.06						1.08 ± 0.05
V	1.29 ± 0.18		1.46 ± 0.22	1.39 ± 0.08				1.38 ± 0.07
Y			1.17 ± 0.11					1.17 ± 0.11
Yb	1.28 ± 0.15							1.28 ± 0.15
Zn	1.25 ± 0.08	1.22 ± 0.09	1.38 ± 0.10	1.18 ± 0.10				1.26 ± 0.05
Zr			1.16 ± 0.08	1.00 ± 0.10				1.10 ± 0.06

*Deleted from error weighted average.

INAA - Instrumental Neutron Activation Analysis
RCAA - Radiochemical Neutron Activation Analysis
XRF - X-Ray Fluorescence Analysis

PES - Plasma Emission Spectroscopy (Sodium Carbonate Fusion)
FAA - Conventional Flame Atomic Absorbtion (Lithium Metaborate Fusion)
GFAA - Graphite Furnace Atomic Absorbtion
CVAA - Cold Vapor Atomic Absorbtion

TABLE 4. RETORTED/RAW SHALE RATIO SUMMARY FOR NONVOLATILE ELEMENTS
PARAHO OIL SHALE COLLECTION 8/24/77

Method	Error Weighted Average	Unweighted Average Error <5%
INAA	1.20 ± 0.01 (32)*	1.20 ± 0.02 (14)
XRF	1.24 ± 0.02 (20)	1.21 ± 0.05 (4)
PES	1.17 ± 0.01 (15)	1.18 ± 0.04 (8)
FAA	1.19 ± 0.01 (8)	1.21 ± 0.05 (7)
Overall	----	1.20 ± 0.019 (33)

* Number in () is number of measurements used in average.

INAA = Instrumental Neutron Activation Analysis
XRF = X-ray Fluorescence (Energy Dispersion)
PES = DC-Coupled Plasma Emission Spectroscopy
FAA = Conventional Flame Atomic Absorption

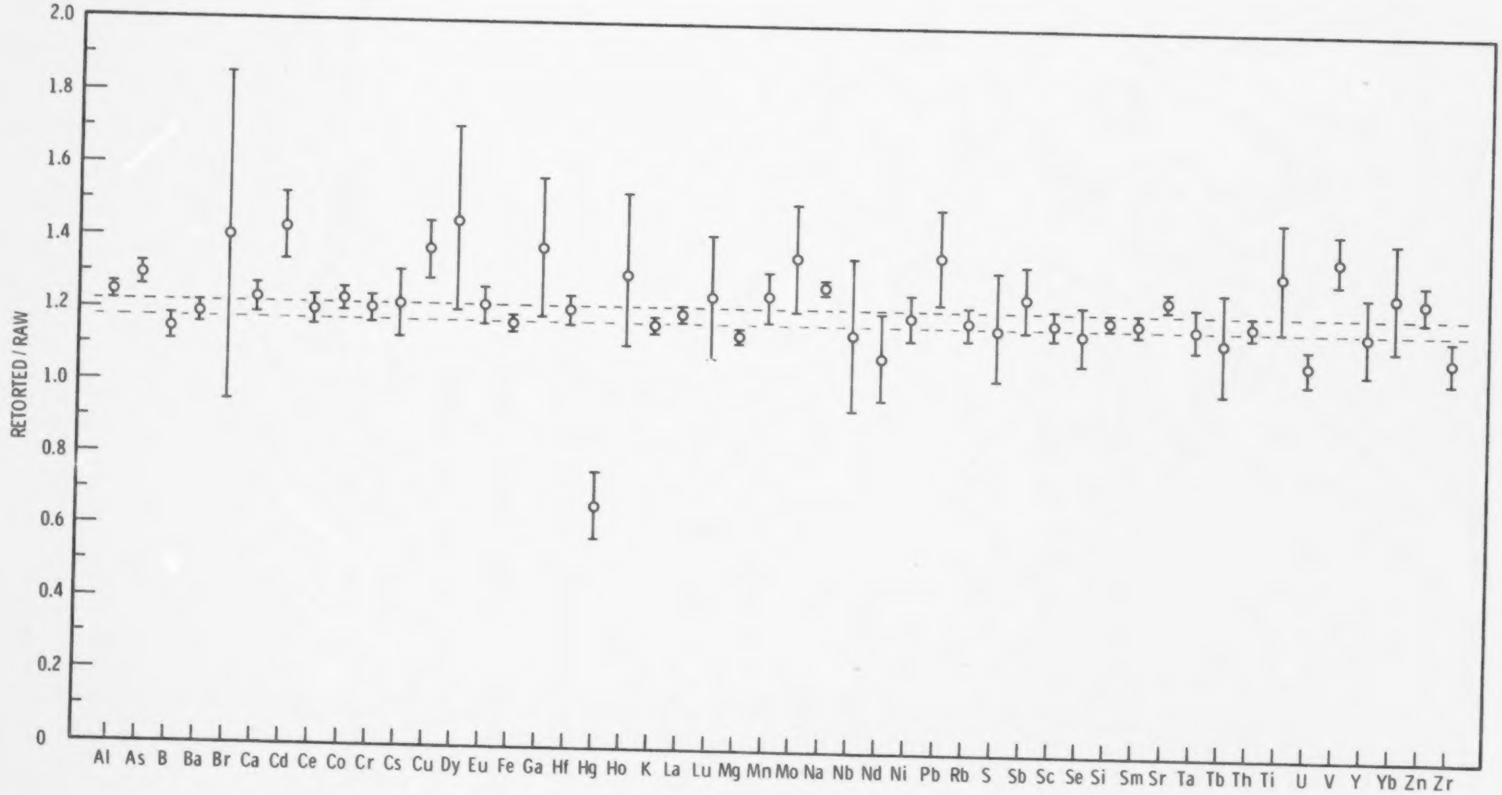
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
RETORTED / RAW
Al As B Ba Br Ca Cd Ce Co Cr Cs Cu Dy Eu Fe Ga Hf Hg Ho K La Lu Mg Mn Mo Na Nb Nd Ni Pb Rb S Sb Sc Se Si Sm Sr Ta Tb Th Ti U V Y Yb Zn Zr

Figure 3.

Table 5 . Percentage of Elements Transfered From Feedstock Raw Shale to Product Oil

(8-24-77)

Element	Abundance In Raw Shale, ppm	Abundance In Product Oil, ppm	% Element Transfered From Raw Shale To Product Oil
H	15,000	117,000	65.4
C	155,000	860,000	46.5
N	6,600	23,900	30.3
S	6,000	7,400	10.4
Hg	0.089	0.30	28.2
As	44	31	5.9
Se	2.0	0.91	3.8
Co	9.0	0.93	0.87
Ni	28	2.74	0.82
Sb	2.1	0.028	0.11
Cu	40	0.42	0.088
Zn	64	0.41	0.054
V	94	0.25	0.022
Fe	20,700	49	0.020
Th	6.3	0.009	0.012
Ti	1,800	2.6	0.012
Mg	34,600	25	0.0061
Mn	315	0.21	0.0056
Al	37,700	16	0.0036
Ca	101,000	42	0.0035
Si	150,000	55	0.0031
Na	16,900	4.3	0.0021

Table 6. Percentage of Elements Transfered From Feedstock Raw Shale to Product Water

(8-24-77)

Element	Abundance In Raw Shale, ppm	Abundance In Product Water, ppm	% Element Transfered From Raw Shale To Product Water
H	15,000	105,000	2.7
S	6,000	39,000	2.5
Se	2.0	9.8	1.9
N	6,600	23,000	1.3
B	94	43	0.18
C	155,000	25,000	0.062
As	44	5.7	0.050
Hg	0.089	0.0023	0.010
Ni	28	0.54	0.0074
Cu	40	0.70	0.0067
Mg	34,600	490	0.0055
Sb	2.1	0.020	0.0037
Mo	22	0.15	0.0026
Na	16,900	111	0.0025
Zn	64	0.41	0.0025
Co	9.0	0.03	0.0013
Ti	1,800	5.1	0.0011
Rb	75	0.14	0.00072
Sr	700	0.85	0.00048
Mn	315	0.18	0.00022
V	94	0.045	0.00018
Ca	101,000	38	0.00015
Si	150,000	41	0.00011
Fe	20,700	1.5	0.000028

TABLE 7. PERCENTAGE OF ELEMENTS TRANSFERRED FROM FEEDSTOCK RAW SHALE TO PRODUCT GAS

Element	Abundance in Raw Shale, ppm	Abundance in Product Gas	% Element Transferred from Raw Shale to Product Gas
H	15,000	26.7 (g/m^3)	40.0
C	155,000	146.0 (g/m^3)	21.1
N	6,600	5.4 (g/m^3)[1]	17.9
S	6,000	3.4 (g/m^3)	12.7
Hg	0.089	75.0 ($\mu g/m^3$)	23.0
As	44	155.0 ($\mu g/m^3$)	0.079

---

[1] N as NH_3

Zn. While they were not detected in the product oil, water, or gas, three additional elements, Mo, Pb, and U, cannot be ruled out as members of this group due to their detection limits. The third category (III) is characterized by the elements which have greater than 10% of their mass redistributed into products other than the retorted shale. This group includes the major elements C, H, N, and S, and the volatile heavy metal Hg.

The redistribution of category I elements into the product oil is primarily in the form of raw and/or retorted shale fines. This statement is based on data in Table 5, which tabulates the partitioning coefficients for all elements detected in the product oil. The partitioning coefficients for the mineral elements Al, Ca, Mg, Mn, Na, and Si ranged from 0.0021 to 0.0061% with a mean and relative standard deviation of 0.0040 ± 0.0015%. The small but essentially equal fractions of these six elements in the product oil indicate that they are most likely being redistributed together as shale particulate matter.

If the base level of elements associated with shale particulates in the product oil is set equal to the mean value calculated above (0.0040%) plus two standard deviations (0.0030%), it is reasonable to conclude that elements with partitioning coefficients exceeding the sum (0.007%) are present in additional chemical forms. Analytical errors or sample contamination may invalidate this statement for a few elements close to the 0.007% limit (e.g., Ti and Th); however, for elements with partitioning coefficients of 0.02% or greater (e.g., Fe), this difference is considered to be real. The elements of category II are probably redistributed as volatile metallic or organo-mettalic compounds. This statement is supported by other mass balance studies (Fox et al., 1977; Chendrikar and Faudel, 1978) and by investigations which report that As and Fe (Sullivan et al., 1977) cannot be removed from Paraho shale oil filtered through 15-micron filters. An additional explanation is that very fine grained and insoluble trace minerals, chemically unlike the shale fines, are being preferentially precipitated or transported into the product oil.

The observed redistribution of Category III elements into the product oil ranged from 10.4% for S to 65.4% for H. A significant fraction (30.3%) of the trace element Hg was observed to partition into the product oil. This partitioning coefficient agrees well with others reported for Hg in various oil shale retorting processes (Fox et al., 1977) and in laboratory retorting studies (Donnell and Shaw, 1977).

The abundances and partitioning coefficients for elements detected in the product water are summarized in Table 6. Because the August 24 water sample was collected from one of the small gauging tanks, it represented product water which had only recently been coproduced by the retorting process. Other more "aged" product waters were collected on August 26 and November 15 and 16 from the large settling tanks used for oil-water separation. The product water obtained from these tanks is typically several days older than water in the gauging tanks.

The partitioning coefficients for S and Se in the August 24 product water are 2.5 and 1.9%, respectively. This rather close agreement may be related to the elements' chemical similarities. The total S measured in the product water was 3.9%; however, the $S^=$ levels were only a few ppm. About 0.05% of the raw shale As was observed to partition into the product water. The chemical form of the arsenic in the product water is about 50% As^{+3} and 50% As^{+5}. No methyl or dimethyl arsenic was detected.

The abundances and partitioning coefficients for elements detected in the product gas are summarized in Table 7. Significant fractions of the elements C, H, Hg, N, and S are released from the raw shale and redistributed into the product gas. In addition, a small fraction of the As (0.08%) was also observed to partition into the gas. The element hydrogen is redistributed in the gas chiefly as water vapor, H_2, CH_4, and other hydrocarbon gases. Carbon is redistributed as hydrocarbon gases, as CO and CO_2 from combustion, and as CO_2 from decomposition of the carbonate minerals. Nitrogen is redistributed as NH_3 and other nitrogen species in the gas phase.

The partitioning coefficient for total sulfur redistributed into the product gas was observed to be 12.7%. The partitioning coefficient for Hg in the gas was observed to be 23.0%. The chemical form is assumed to be elemental mercury vapor (Hg^o) as organic forms should be condensed with the product oil. The small fraction of arsenic in the product gas was primarily inorganic AS_2O_3 vapor. Only a small quantity of arsine or methylated arsine was detected.

SUMMARY AND CONCLUSIONS

In organic analysis of solid, liquid and gaseous samples from the Paraho Semiworks Retort were completed using a multitechnique approach. Most of the techniques used instrumental methods, so that interferences from chemically complex matrices could be minimized. In many cases, analytical techniques were altered or improved in order to make them applicable to oil shale samples.

The data were statistically analyzed to determine both the precision of each method and to see how closely the various techniques compared. The data were also used to determine the redistribution of 31 trace and major elements in the various effluents, including the offgas for the Paraho Retort operating in the direct mode. The computed mass balances show that approximately 1% or greater fractions of the As, Co, Hg, N, Ni, S and Se are released during retorting and redistributed to the product shale oil, retort water or product offgas. The fraction for these seven elements ranged from almost 1% for Co and Ni to 50-60% for Hg and N.

Approximately 29% of the S and 5% of the As and Se are released. The mass balance redistribution during retorting for Al, Fe, Mg, V and Zn was observed to be no greater than 0.05%. These redistribution figures are generally in agreement with previous mass balance studies made for a limited number of elements on laboratory or smaller scale pilot retorts (Fox et al., 1977; Shrendrikar and Gaudel, 1978; Wildeman, 1977; Fruchter et al., 1978). Thus, the mass balances reported here for the Paraho Retort may have some general validity for other types of oil shale retorting technologies.

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APPLICATIONS OF DISSOLVED ORGANIC CARBON FRACTIONATION ANALYSIS TO THE CHARACTERIZATION OF OIL SHALE PROCESSING WATERS

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ABSTRACT

Dissolved organic carbon (DOC) fractionation analysis is a method which separates and quantitates organic solutes dissolved in water into hydrophobic acid, base, neutral, and hydrophilic acid, base, neutral compound classes. Analytical-scale DOC fractionation, which gives DOC distribution of the six solute fractions, has been used to determine changes in organic-solute composition of surface and groundwater with input of oil shale processing water. Preparative-scale DOC fractionation, which generates organic solute fractions for further study, has been used for characterization of organic solutes in oil shale processing waters, and, through a modification utilizing activated carbon, has been used to prepare gram-sized fractions for biological testing of organic solutes in oil shale processing water. Both analytical and preparative-scale DOC fractionation were used to study sorption of organic solutes from oil shale processing waters on processed-shale and soil sorbents to predict the transport of these solutes in surface and groundwater systems.

INTRODUCTION

Methodology for dissolved organic carbon (DOC) fractionation analysis was recently developed at the National Water Quality Laboratory (U.S. Geological Survey) (Leenheer and Huffman, 1976) to serve as an organic-compound class analysis that fills the gap in organic-solute characterization between organic-solute concentration in water (DOC) and specific compound analysis. The fractionation is based on physical adsorption of hydrophobic solutes on a nonionic, acrylic-ester macroreticular resin, and ion-exchange adsorption of hydrophilic solutes. Six characteristic fractions (hydrophobic acids, bases, neutrals, and hydrophilic acids, bases, neutrals) are obtained at the end of the fractionation procedure. The procedure is quantified by organic-carbon analysis of the various fractions.

Since its inception, DOC fractionation analysis has generally been used in two different manners. (1) Analytical-scale DOC fractionation which determines the sixfold separation of DOC in water into various compound classes, can be performed on a small (200-mL) water sample whose DOC content is 5-25 mg/L and whose specific conductance is less than 2,000 μmhos/cm at 25°C. A standard method for analytical-scale DOC fractionation is published (Leenheer and Huffman, 1979). (2) Preparative-scale DOC fractionation is used to generate gram-sized organic solute fractions for additional study and characterization; no standard method is intended for preparative-scale DOC fractionation because of the highly variable nature of research objectives for organic-solute fractions isolate from water.

Use of DOC fractionation analysis and its various modifications is most valuable when the research objective is to obtain intermediate-level qualitative and quantitative information about the nature of organic solutes dissolved in water. It provides the basis for a phramidal classification of organic solutes in water, beginning with DOC at the pyramid apex, and ending with each specific organic compound at the pyramid base (Leenheer and Huffman, 1976, p. 739). DOC fractionation analysis is also very useful for quantitative determination, isolation, and study of high molecular-weight natural organic polyelectrolytes, which constitute the bulk of organic carbon dissolved in natural surface and groundwaters (Malcolm, Thurman, and Aiken, 1977).

Oil shale processing is accompanied by coproduction of wastewaters which are heavily laden with organic and inorganic constituents. Wastewater production is particularly significant for in situ oil shale processing. A recent report (Farrier and others, 1978) describes the sources and amounts of waters derived from in situ processing and summarizes water-related research being conducted by the Laramie Energy Technology Center (U.S. Department of Energy). This research includes management, treatment, and utilization of process waters. Environmental studies include their effects on biological systems, their characterization, and their disposition, transport, and fate in the environment. DOC fractionation analysis has been applied in many of these studies and has been proven a useful analytical approach toward characterization of organic-solutes in process-derived waters.

The purpose of this report is to cite and evaluate applications of DOC fractionation analysis to characterization of oil shale processing waters. The use of DOC fractionation analysis for determining the nature of sorptive interactions of process waters with processed shale and soil sorbents will also be discussed.

DISCUSSION OF EXPERIMENTAL PROCEDURES

Analytical-Scale DOC Fractionation of Oil Shale Processing Waters

A description of the standard method for analytical-scale DOC fractionation is under preparation and should be published in the near future (Leenheer and Huffman, 1978). The flow chart for this analytical scheme is given in Figure 1.

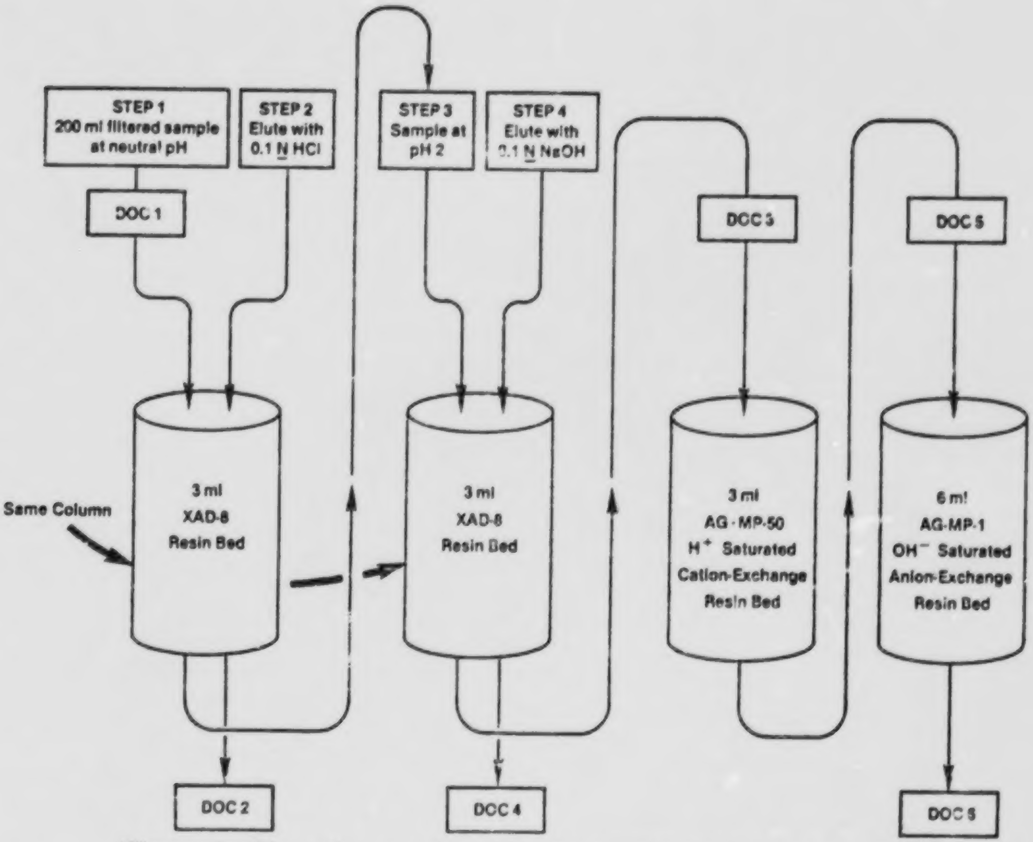


Figure 1. Flow diagram for analytical-scale DOC fractionation.

Water samples for DOC fractionation should be filtered through a 0.45 μm silver membrane or glass fiber filter before they are processed. Passage of a water sample through the three columns is a two-step process. It is first passed through the XAD-8 column; then, after the hydrophobic base fraction is eluted and the sample pH is adjusted, it is passed through all three columns in series. Desorption of the hydrophobic-acid fraction and collection of sample aliquots for DOC analysis at various points in the flow scheme of Figure 1 constitute the remainder of the procedure. All DOC analyses should be performed with a carbon analyzer whose limit of detection is 0.1 mg/l. Oil shale processing waters typically contain high concentrations of organic solutes (500-20,000 mg/l DOC); they should be diluted with distilled water before the fractionation is performed, until the DOC is near 25 mg/l. This dilution is required for the following reasons: (1) high organic-solute concentration lead to ion-pair formation between organic acids and bases, which results in acids in base fractions and bases in acid fractions; (2) high inorganic-solute concentrations enhance the adsorption of organic-inorganic acid and base salts; as a result, the separation between organic and inorganic solutes is decreased; (3) acidification of oil shale processing waters frequently produce elemental-sulfur precipitates which foul the resin adsorbents (Stuber and Leenheer, 1978A); sulfur-precipitate formation is almost eliminated if DOC fractionation is performed on highly-diluted process water; (4) organic-solute distribution coefficients change when a resin adsorbent becomes "saturated" at high solute concentrations.

Preparative-Scale DOC Fractionation of Oil Shale Processing Waters

For most applications, analytical-scale DOC fractionation cannot be used as a preparative procedure because the quantity of each fraction desired (10 mg-10g) requires the use of prohibitively large volumes of diluted samples and large columns of resin adsorbents. A compromise must be struck between diluting to the "ideal" conditions of the analytical-scale fractionation versus no dilution, with all of the attendant problems discussed previously. As most of the solute-solute and solute-resin interactions occur in the hydrophobic-solute fractions, an assessment of these interactions can be determined by passing a process water at various dilutions through columns of XAD-8 at a fixed ratio of water to resin adsorbent, without "saturating" the resin and monitoring the DOC adsorbed versus dilution. Table 1 shows the effect of dilution on hydrophobic DOC adsorption of an oil shale processing water obtained from the 150-ton simulated *in situ* retort of the Laramie Energy Technology Center (Run 13, Barrel 66). At the 100 and 1,000-fold dilution level, hydrophobic DOC adsorption was independent of concentration, whereas at the 0 and 10-fold dilution level there was a high dependence. Based on the results of Table 1, considerations of water volumes (<40 L), resin quantities (<4 L), and the fraction quantities desired (1-3 g organic carbon), the 10-fold dilution factor (DOC=507) was chosen for preparative-scale fractionation. Variability in amounts and types of solutes found in different process waters (Jackson and others, 1975; Fox and others, 1978) will require this type of preliminary evaluation for each study sample.

TABLE 1. ADSORPTION OF HYDROPHOBIC DOC FROM 150-TON RETORT WATER ON XAD-8 VS DILUTION FACTOR

Dilution Factor	DOC	Percent DOC Adsorbed	Percent DOC Eluted
0	5,070.0	59.8	40.2
10	507.0	40.2	59.8
100	50.7	31.8	68.2
1,000	5.07	32.2	67.8

A second major problem with preparative-scale DOC frationation of oil shale processing waters is formation of sulfur precipitates when these waters are acidified. Removal of the elemental sulfur precipitate by filtration or centrifugation is not a good approach, because sulfur is a good adsorbent for hydrophobic organic acids, and a substantial portion of this fraction is removed with the sulfur. The approach used was to convert sulfur-forming precursor thiosulfate to tetrathionate, by titration of the sample with a stoichiometric quantity of sodium tri-iodide. Acidification of the titrated sample did not cause any precipitates to form.

The final major difficulty with preparative-scale DOC fractionations of oil shale processing waters is high concentration of carbonate and bicarbonate species in these waters. When most of the anions were carbonates and bicarbonates, it is advantageous to modify the sample-flow schem of DOC frationation, so the water is acidified by passage through hydrogen-saturated ion-exchange resin, instead of by NCl addition. The ion-exchange resin converts carbonates and bicarbonates to CO_2 gas. A much smaller amount of anion exchange resin is required in the next column if the carbonate and bicarbonate equivalents have been removed as CO_2 in the cation exchange column, rather than being replaced by chloride equivalents which must later be removed on anion-exchange resin. To remove carbon-dioxide gas, a T was placed in the sample delivery tube at the head of the column, and the CO_2 was drawn off the column headspace by a vacuum generated by a water asperator. If the cation-exchange column is greater than 5 cm in diameter, CO_2 gas that froms will rise in bubbles through the exhausted portion of the resin bed until it collects in the headspace area. With small diameter columns, CO_2 gas moves downward through the column, disturbs the flow, and diffuses the reaction front which decreases the resolution of the solute separation.

The flow scheme finally devised for preparative-scale DOC frationation of a sample of processing water from the 150-ton oil shale retort is shown in Figure 2. Preparative-scale DOC fractionation is quantified by organic-carbon analysis of the sample stream at each step. Recoveries of the various fractions from the resin sorbents are determined by comparing organic carbon adsorbed vs organic carbon desorbed in each eluent. Five of the fraction eluents are in water, and DOC can be determined by a number of standard procedures. However, the hydrophobic neutral fraction is dissolved in methanol (Casterline and Leenheer, 1978). Recoveries of hydrophobic-solute fractions are essentially quantitative from the XAD-8 resin; however, recoveries vary between 60 and 80 percent for the hydrophilic bases and acids from ion-exchange resins.

Preparation of Fractions for Study of Biological Effects

A modified preparative-scale DOC fractionation was recently developed by Huffman (1979) to generate organic-solute fractions suitable for delineation of toxic materials in conjunction with evaluating biological effects of *in situ*-produced waters (Farrier and others, 1978). The preparative-scale methodology discussed previously is unsuitable because it may induce changes in a sample during pH adjustment; certain fractions were in solvents unsuitable for testing; and too many fractions were obtained by the procedure for use in the testing program. An *in situ* oil shale processing water designated Omega 9 (Farrier and others, 1977, 1978) was fractionated by this modified procedure. A flow-chart of the procedure is given in Figure 3. The procedure was quantified by organic-carbon analysis of the sample flow stream and the column eluents.

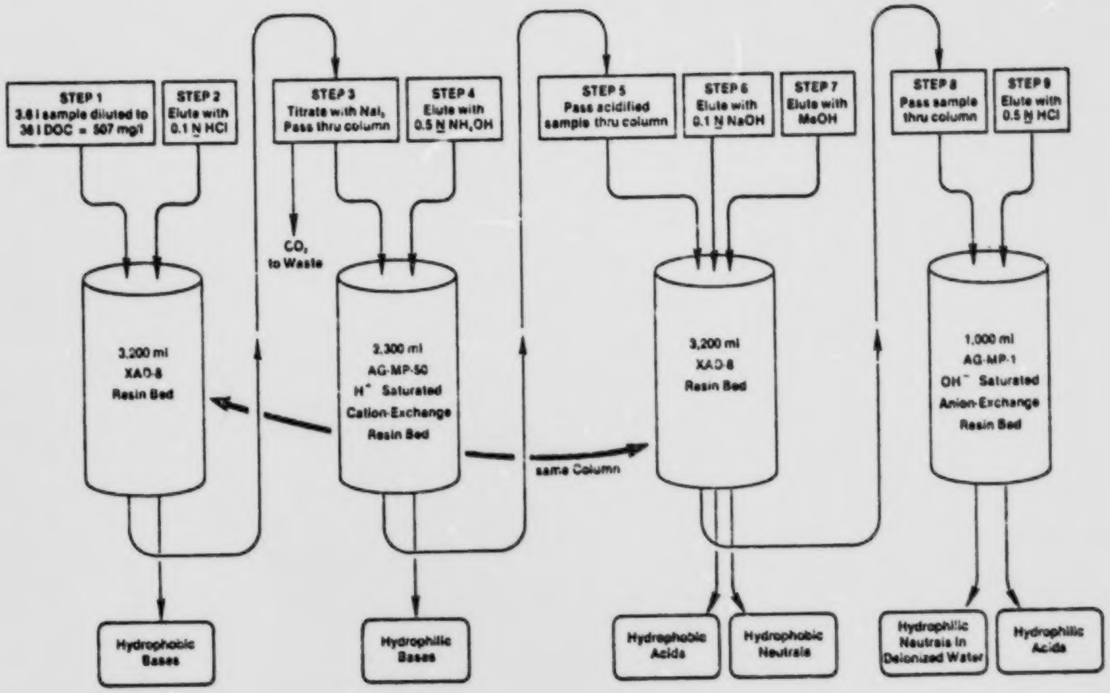
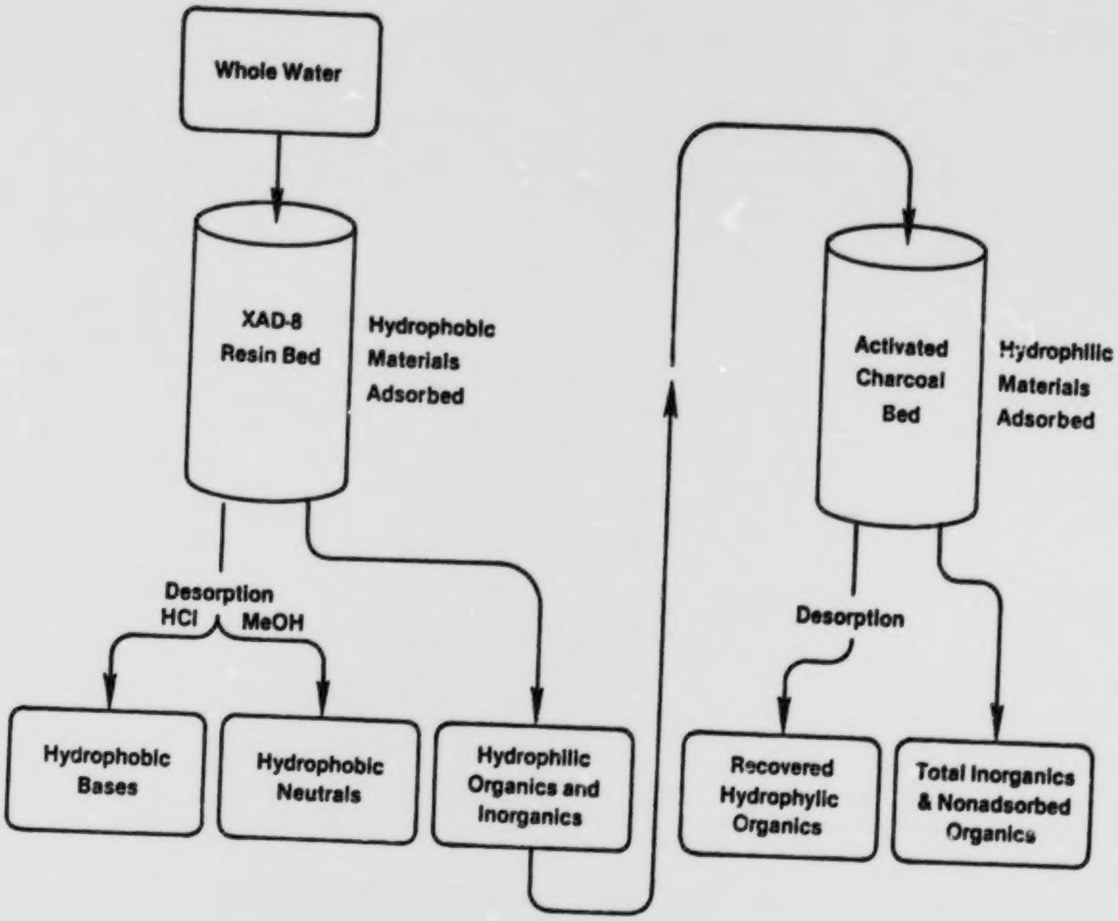


Figure 2. Flow diagram for preparative-scale DOC fractionation of oil shale processing water.


Whole Water
XAD-8 Resin Bed
Hydrophobic Materials Adsorbed
Desorption
HCl
MeOH
Hydrophobic Bases
Hydrophobic Neutrals
Hydrophilic Organics and Inorganics
Activated Charcoal Bed
Hydrophilic Materials Adsorbed
Desorption
Recovered Hydrophylic Organics
Total Inorganics & Nonadsorbed Organics

Comparison of DOC Fractionation Procedures

A basis for comparison of various DOC fractionation procedures is provided by analytical-scale DOC fractionation. After the organic-solute concentration of a water sample is diluted to DOC ≤ 25 mg/L, the hydrophobic-hydrophilic separation is mainly dependent on the distribution coefficient k', for organic-solutes sorption on SAC-8 resin. The column distribution coefficient k', and its relation to the mass distribution coefficient D_m, is shown as follows:

$$k' = \frac{\text{mass of solute sorbed on XAD-8}}{\text{mass of solute dissolved in water}}, \qquad (1)$$

$$D_m = k' \frac{\text{ml of water}}{\text{g of XAD-8}} . \qquad (2)$$

In analytical-scale DOC fractionation, the experimental procedure is defined so organic solutes that sorb in the nonionic state, whose k' are $\geq$ than 110 are termed hydrophobic, and those whose k' are <110 are termed hydrophilic (Leenheer and Huffman, 1979). A listing of k' values for various organic standard-compound sorption on XAD-8 is given in a report by Thurman, Malcolm, and Aiken (1978).

An oil shale processing water from the 150-ton simulated *in situ* retort and the *in situ* "Omega 9" oil shale processing water were fractionated by both preparative-scale and analytical-scale procedures; results are presented in table 2. The major difference between these preparative-scale and analytical-scale DOC fractionations is the increase in the percentage of hydrophobic solutes for preparative-scale fractionation. This difference was expected because the lower ratio of sample volume to XAD-8 resin in preparative-scale fractionation gave a hydrophobic: hydrophilic break at a k' of 110 for analytical-scale fractionation. Most of the change going from analytical-scale to preparative-scale fractionation is caused by conversion of hydrophilic acid and base solutes to hydrophobic-neutral solutes. The solute-solute and solute-resin interactions discussed previously, along with the differenc in k' break, are believed to cause the changes in preparative-scale fractionation. Because these changes in preparative-scale fractionation are an undesirable departure from fractionation produced by analytical-scale procedure, additional purification of individual solute fractions obtained from preparative-scale fractionation is often necessary. For example, the hydrophobic base fraction can be purified of most undesirable solute species by another cycle of adsorption and desorption on XAD-8 resin.

A comparison of preparative-scale fractionation modified for biological-effects testing (Figure 3) vs analytical-scale DOC fractionation of Omega 9 water was given in the report by Huffman (1979). The results are given in Table 3.

Two major changes of the modified preparative-scale procedure are omission of sample acidification and recycle through XAD-8, and substitution of activated carbon for ion-exchange resins. The effect of not acidifying the sample was assessed by omitting this step in an analytical-scale fractionation. The effect, as shown in Table 3, was to shift most of the hydrophobic acids into the hydrophilic-acid fraction. Altering the procedure from analytical-scale fractionation without sample the pH adjustment to modified-preparative scale fractionation, increased the hydrophobic solute percentage (as discussed in the previous section of this report). The "carbon-adsorbable" fraction and "nonadsorbable" fraction of modified preparative-scale fractionation were characterized by redissolving these fractions in water and performing an analytical-scale DOC fractionation on each fraction. The "carbon adsorbables" consisted mainly of hydrophobic acids, hydrophilic acids, and hydrophilic neutrals, whereas the "nonadsorbables" consisted mostly of hydrophilic acids and neutrals. The main

TABLE 2. PREPARATIVE-SCALE VS ANALYTICAL-SCALE DOC FRACTIONATIONS IN PERCENT OF DOC

Fraction	150-ton Retort Water DOC=5,000 mg/L		Omega 9 Retort Water DOC=1,000 mg/L	
	Analytical-Scale Fractionation	Preparative-Scale Fractionation	Analytical-Scale Fractionation	Preparative-Scale Fractionation
Hydrophobic solutes	55	65	49	61
Hydrophilic solutes	45	35	51	39
Hydrophobic bases	9	9	13	14
Hydrophobic acids	26	28	19	18
Hydrophobic neutrals	20	28	17	29
Hydrophilic bases	15	8	12	9
Hydrophilic acids	23	17	29	15
Hydrophilic neutrals	8	10	10	15

TABLE 3. MODIFIED PREPARATIVE-SCALE VS ANALYTICAL-SCALE DOC FRACTIONATIONS FOR OMEGA 9 WATER IN PERCENT OF DOC

Fraction	Analytical-Scale Fractionation	Analytical-Scale Fractionation without Sample pH Adjustment and Recycle Step	Modified-Preparative-Scale Fractionation
Hydrophobic solutes	49	34	38
Hydrophilic solutes	51	66	62
Hydrophobic bases	13	13	16
Hydrophobic acids	19	4	--
Hydrophobic neutrals	17	17	22
Hydrophilic bases	12	12	Carbon adsorbables = 47
Hydrophilic acids	29	46	Nonadsorbables = 15
Hydrophilic neutrals	10	8	--

limitation of this modified preparative-scale fractionation scheme is low recovery (32 percent) of the carbon-adsorbable fraction.

APPLICATIONS OF DOC FRACTIONATION ANALYSIS

Various developments in, and modification of, DOC fractionation analysis have led to many diverse applications of the methodology. Most applications have been in characterization of oil shale processing waters, and the data is being considered to develop guidelines for control-technology aspects of environmental research dealing with oil shale processing.

Water Quality Monitoring

A recent report by Stuber and Leenheer (1978B) assessed analytical-scale DOC fractionation as a water quality monitoring parameter for inputs of oil shale processing water into natural surface waters. Several natural surface waters from the White River Basin in Eastern Utah were characterized by DOC fractionation analysis. Inputs of oil shale processing water into these surface waters would change the hydrophobic base fraction significantly. The authors concluded that inputs into natural surface waters of less than one part of 250 of Omega 9 processing water, or one part in 1,000 of 150-ton processing water could be detected by DOC fractionation. Changes in the other five fractions were not sufficiently diagnostic to justify a monitoring program utilizing the complete DOC fractionation, so they suggested using only the hydrophobic base fraction for monitoring processing water inputs into surface waters.

Changes in groundwater quality determined by DOC fractionation as a result of *in situ* oil shale processing are given in another report by Stuber and Leenheer (1978A). Analytical-scale DOC fractions were performed on groundwater withdrawn from the Rock Springs Site 9 *in situ* retort of the Laramie Energy Technology Center (Long and others, 1977) before retorting, during retorting (Omega 9), and one year after retorting. These DOC fractionations give characteristic fraction ratios for organic-solute distributions in the natural groundwater, the Omega 9 process water, and of most interest, the degree of mixing of natural organic solutes with process-derived organic solutes one year after the burn. More than one-half of the organic solutes from water withdrawn from Site 9 production wells one year after the burn were natural organic solutes from incursive groundwater.

Organic Solute Sorption Studies

DOC fractionation analysis is an excellent method for studying organic-solute sorption phenomena from complex solute mixtures, such as oil shale processing water upon heterogeneous sorbent surfaces, for example, soil, sediment, and processed shale. Both preparative-scale and analytical-scale fractionations can be used to define and quantify the affinity of various solute fractions for a sorbent, and this information can be used in organic-solute transport models for oil shale processing water movement in surface and groundwater systems.

The preparative-scale fractionation method presented in Figure 2 was used to generate organic-solute fractions for sorption isotherm studies of 150-ton retort processing water on processed shale from the TOSCO II process (Stuber and Leenheer, 1978A). TOSCO II processed shale was found to have a greater affinity for organic-acid fractions than organic-base fractions, and greater affinity for hydrophobic fractions compared with respective hydrophilic fractions.

Analytical-scale fractionation is presently used to assess sorptive interactions of Omega 9 processing water with soil sampled on Site 9. In this procedure, a sorption isotherm of unfractionated processing water is run for various concentrations of soil; after sorption is complete, an analytical-scale DOC fractionation is run on the solution phase of each soil-water mixture. Preliminary results indicate that organic-base fractions are sorbed preferential to organic-acid fractions using soil as a sorbent; that is the reverse case to using TOSCO II processed shale as the sorbent. Omega 9 processing water also acts to extract significant amounts of natural organic solutes from soil organic matter; thus, an independent determiantion of DOC fractionations of these extractable solutes must be made for various soil-water mixtures to correct sorption isotherm data. It is the opinion of the authors that use of analytical-scale fractionation for assessment of sorption phenomina is more accurate than use of preparative-scale fractionation because: (1) all sample matrix effects are present when the sorption isotherm is run using unfractionated processing water; and (2) analytical-scale DOC fractionation is higher in accuracy than preparative-scale DOC fractionation.

Organic-Solute Characterization of Oil Shale Processing Waters

Organic-solute characterization of oil shale processing water by DOC fractionation can range from the use of DOC fraction ratios as diagnostic indicators to generation of organic-solute fractions on which specific compound analyses can be performed. DOC fraction ratios are useful to compare organic-solute class distributions in various oil shale processing waters, natural surface waters, and natural groundwaters.

Some preliminary compound identification has been performed on hydrophobic-base, hydrophobic-acid, and hydrophilic-acid fractions prepared by preparative-scale fractionations of Omega 9 and 150-ton retort processing waters. By using the techniques of GC-elemental analysis and GC-UV analysis, pyridine, aniline, quinoline, and mono-, di-, and trimethyl pyridines were determined in hydrophobic-base fractions. Fatty acids from C_1 to C_3 were found in hydrophilic-acid fractions; and fatty acids from C_3 to C_8 were in the hydrophobic acid fraction. Fatty acids greater than C_8 stay on XAD-8 resin even in the ionized state are found in the hydrophobic-neutral fraction.

Performing a preparative-scale DOC fractionation preliminary to gas-chromatographic or liquid-chromatographic analysis gives the analytical advantage of having relatively-homogeneous organic solute fractions for which it is relatively easy to select the correct chromatographic column-packing. Another significant advantage is knowledge of the quantitative DOC fractionation and DOC concentrations in each solute fraction. If only microgram quantities of organic solutes are needed in each fraction for GC or LC analysis, analytical-scale DOC fractionation can also serve as preparative-scale fractionation.

SUMMARY AND CONCLUSIONS

In the two years since the origination of DOC fractionation analysis, this analytical methodology has been applied to oil shale processing water characterization in the areas of water quality monitoring of processing water inputs to surface and groundwaters; interpretation of organic-solute sorption-phenomena on soil, sediment, and processed shale sorbents; characterization of organic-solute content of oil shale processing water; and generation of organic-solute fractions for use in biological-effects testing programs. Because DOC fractionation analysis is new, much additional fundamental research to define organic-solute composition of each fraction, and to understand competitive sorption phenomena in complex solute mixtures is in progress. DOC fractionation analysis has provided much useful intermediate-level qualitative and quantitative information on organic-solute composition of oil shale processing waters, and natural surface and groundwaters which these processing waters may impact.

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SAMPLING STRATEGIES IN GROUNDWATER TRANSPORT AND FATE STUDIES FOR *IN SITU* OIL SHALE RETORTING

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ABSTRACT

This paper proposes a new concept for designing groundwater monitoring programs to assess the effects of *in situ* oil shale retorting. The concept includes new ways to characterize pollution source terms, build and calibrate hydrological models, estimate stochastic systems, and optimize measurement system designs. The solution to the monitoring problem would be the minimum-cost program that estimates pollutant concentrations throughout the groundwater region within an acceptable error criterion. That program would specify the lowest number of wells that need to be drilled, their best locations and depths, and how seldom they need by sampled. The approach can be applied to meet differing requirements of characterizing regional hydrology, studying geochemistry, determining pollutant transport and fate, and designing monitoring networks to demonstrate compliance with effluent regulations.

INTRODUCTION

Millions of dollars have been spent on programs to monitor groundwater in assessing the effects of extracting energy by *in situ* oil shale retorting. Not all of these programs have yielded useful data for decision makers and environmental planners. The purpose of this paper is to propose a new concept in rationally designing groundwater monitoring systems. The concept combines new techniques available in source term characterization, hydrological modeling, stochastic system estimation, and dynamic systems theory in a new way to approach the solution of the problem of how to

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monitor groundwater. The solution would be a minimum-cost monitoring program that yields best estimates of groundwater pollutant concentration. To estimate pollutant concentrations throughout the groundwater region within an acceptable error criterion, that program would specify the most advantageous locations and depths of measurement wells, the lowest number of wells that need to be drilled, how seldom samples need be taken from those wells, and what types of samples should be obtained.

The need for this new approach seems clear. We will briefly summarize some of the remarks from related papers given at this symposium that substantiate the need for our new approach to monitoring groundwater.

Douglas Skie, the Quality Assurance Coordinator for EPA Region VIII, outlined minimum requirements for oil shale environmental sampling quality assurance programs at this symposium.[1] He subsequently mailed to symposium participants several EPA documents describing various aspects of regional implementation plans for quality assurance programs. One of these documents, entitled Minimal Requirements for a Water Monitoring Quality Assurance Program,[2] outlines a minimum quality assurance program the EPA regions are requiring states to comply with to receive certain Federal EPA grants under a 1976 law. The document includes detailed sections on general water chemistry, water chemistry specific to organics, water microbiology, field sampling, and data handling.

What is notable about this report is that it contains a wealth of detailed information on chemistry and data handling but a dearth of information on sampling network design. The essence of the only remarks on assuring the quality of a design for a sampling network is contained in the following quotation from that report:[2]

> Assurance of representative sampling, both as to site selection and frequency, requires a sampling network design which provides:
>
> 1. A sufficient number of representative sampling locations.
> 2. Types of samples.
> 3. Frequency of sampling.
>
> If properly addressed, these three factors will provide a valid representation of the characteristics being assessed and should insure that program objectives are met.

What is not clear at all in these statements is just how the states are to go about determining the adequacy of the sampling networks to assure the quality of the data they produce. In particular, Skie mentions nothing about the design of the groundwater sampling networks. We believe the vagueness of the one paragraph devoted to those remarks out of that 56-page document demonstrates that a gap exists in the ability to design rational quantitative groundwater monitoring programs. We believe that by approaching the monitoring problem as one in stochastic dynamic systems, definitive statements can be made about the wells--the least numbers needed, their location, and how seldom they need to be sampled--to assure the quality of the data resulting from a monitoring program.

Butch Slawson presented a paper closely related to our paper at this symposium (Slawson and McMillion[3]). In it he outlined the methodology developed by General Electric-TEMPO for designing cost-effective programs for monitoring groundwater. The methodology includes four basic steps: (1) identify and characterize potential groundwater pollutant sources, (2) characterize the location of these sources in their hydrologic framework, (3) assess the mobility of potential pollutants underground, and (4) develop a priority ranking of potential pollutants.[4] He discussed some key issues important in applying this methodology to the complex hydrogeological systems encountered in oil shale developments, i.e., selection of the sampling site, methods of well construction and sample collection and frequency of sampling. All these issues bear heavily on the quality of the data that results from a given monitoring system design. Slawson and McMillion concluded that the assurance of quality data depends on the planning and structured designing of programs as much as on the activities more normally associated with quality control and quality assurance programs. We agree with this conclusion. They also identified a need for detailed hydrogeologic evaluation as an integral part of a monitoring design methodology. We also agree with this need and believe it further supports our premise that stochastic, quantitative methods can now be used to solve the problems of identifying subsurface geohydrologic structure,[5] calibrating and verifying models,[6] and minimizing the cost of monitoring system design.[7]

Thomas Sanders presented an unscheduled paper at this symposium. He called for taking a new view of water quality associated with oil shale developments.[8] The view was that water quality issues must be regarded as stochastic in nature. He presented some examples of how to deal with water quality parameters from a random variable perspective. In a brochure, he describes an entire week-long course to be held July 1979, at Colorado State University, devoted to the design of water quality monitoring networks from a stochastic systems point of view.[9] Surface water will be dealt with in the course, and this reaffirms our contention that significant research is still needed in this area for groundwater systems.

APPROACH

The approach we propose to solve the problem of monitoring groundwater consists of several straightforward steps. The first step is to gather together and analyze existing data for characterizing "source term" relationships of potential pollutants that could be leached out of oil shale during and after retorting. The second is to assess the applicability of existing models of groundwater mass and constituent transport. The third is to select the best optimal estimation scheme from available methods that will apply to groundwater problems. The fourth is to incorporate results from statistical experimental design theory that may apply to solving the problem of what is the optimal groundwater monitoring system. The fifth step is to combine all of the above into a unified, rational computer-based methodology for optimally designing environmental monitoring systems.

STATE-OF-THE-ART

In this section we will review the available techniques in each of the "component" research areas we believe can go together to approach solving the problem of optimal monitoring.

Source Term Characterization

The first step in the design of environmental monitoring techniques is to determine the natures of the potential pollutant sources before attempting to assess their possible effects on the environment. Considerable data exist on the types and quantities of pollutant species that could result from underground retorting and groundwater leaching of spent shale. The controversy surrounding the interpretation of these data was one of the main driving forces behind holding this conference. We are here to learn what we can about existing source term information so that we can incorporate those data into our analysis.

Literature data are abundant already from leaching experiments done by other researchers.[10-13] Some of these data indicate that the major constituents in high concentrations in leachate of spent shale include the following:

Na^+, K^+, NH^+_4, HCO^-_3, $SO^=_4$, Cl^-, F^-, and Total Dissolved Solids (TDS).

Significant amounts of toxic trace elements were also observed and include:

As, B, Hg, Mo, Ni, Pb, and Se.

Complex mixtures of organic compounds are also of concern.

One aspect of data interpretation necessary to design a rational monitoring system is to quantify uncertainty in source-term generation rates. If we extrapolate results from data obtained in experiments to commercial oil shale ventures, errors or variations will be induced in the numbers calculated and the numbers actually observed. This concept of error or uncertainty is central to the development of rational measurement design.[14]

A new method for facilitating well-head sampling was recently described by Garvis and Stuermer.[15] This technique uses a portable instrument package to continuously monitor pH, oxidation/reduction potential, conductivity, and temperature during the time a well is flowed for sample collection. When these parameters stabilize, it is likely that the water being produced from the well head is representative of the water in the formations at depth; this is the time samples for detailed chemical analysis should be taken. This technique relates to some of the needs that arise in sampling oil shale waters cited above in Slawson and McMillion.[3] This well-head sampling system has recently been used in coal gasification experiments to study groundwater transport of organic compounds. Distribution of neutral organic compounds was estimated for underground gasification experiments in northeastern Wyoming by Stuermer et al.[16] Adsorption by the coal seemed to be an important scavenging mechanism that affected resulting organic distribution in groundwater. Laboratory experiments have been carried out by Wang[17] to study certain organics and trace metals by batch and fixed bed methods. Thus, we have experience from field and laboratory studies in related source term and leaching experiments for coal gasification that has direct application to oil shale studies.

Hydrological Models

Solutions to the equations of groundwater motion evolved considerably in the past several years. Before digital computers, analytical approaches to mass transport equations were popular for linear time-invariant descriptions. With the advent of digital computers, differencing schemes were implemented to approximate solutions in time and space. Finite difference methods were used widely to study mass transport in confined and unconfined flow. Recently, finite element methods became very popular in the study of general nonlinear, time-varying, mathematical descriptions of groundwater flow.[18] Many of the methods in use within the U.S. Geological Survey (USGS) were recently summarized in a status report by Appel and Bredehoeft.[19] There it was indicated that extensions were made to include mass and solute transport in some of the more recent work. Chemical reactions and adsorption phenomena were included in some of the implementations. Pimentel[20] summarized many special topics in models now available.

Weeks et al.[21] of the USGS used a method of Bredehoeft and Pinder to analyze baseline and affected hydraulics in the Piceance Basin. The existing data were used to compute regional gradients for potentiometric surface. Hypothetical developments at tracts C-a and C-b were incorporated in their model to demonstrate the effects of dewatering on basin hydrology. The USGS developed transport models that Saulnier and others are using to calculate groundwater and mass and solute transport from the prototype lease tracts to the White River in the Piceance Basin.

Besides that directly in the Piceance Basin, a great deal of work was done for other groundwater applications. These applications include analyzing breakthrough times for geothermal reservoirs with production and reinjection wells; and analyzing pollutant migration associated with in situ coal gasification, migration of radionuclides in groundwater adjacent to underground nuclear test cavities, and the study of the fate of nuclear waste buried in underground repositories.[22-25] Closed form solutions, though lacking the detail and sophistication of the more powerful techniques of finite difference and finite element that apply to the general time-varying non-linear case, can be useful in studying approximate solutions for the general case. These solutions may yield very useful information about how groundwater motion occurs over limited ranges of system variables and parameter values.

Thus, there is a wide range of computer implementations of methods to solve the equations of groundwater mass and solute transport. On one end of this range are the methods for finite difference and finite element that can be made arbitrarily detailed in their spatial resolution. On the other end of the range are the exact solutions that apply to only linear approximations to real world groundwater problems and that, in general, will lack the detail of the more sophisticated discretization schemes. The differences in the ends of this range of methods naturally affect how easy it is to implement and compute the solutions in actual applications. This will be an important consideration in selecting the most appropriate hydrological models for use in designing the optimal monitoring system.

Two criticisms were made of our approach at the symposium. One dealt with the simplicity of the models that we described and how these simple models could not adequately simulate complex hydrogeology. We agree that this is one of the important aspects of needed research in this area and include it in our future research plans for actual monitoring system applications. We have discussed similar problems with John Wilson of MIT.[26] He is interested in basic research in the area of fracture flow for nuclear waste storage applications; his results would likely translate to oil shale studies. The other criticism had to do with our approach being "data rich," requiring significant hydrology and geology data to support the models used. At the outset this is true, but the intent of our approach is to eventually incorporate methods that use available data from existing wells to identify models for flow and transport.[27] These models would then be the basis for determining which other wells were needed to adequately monitor groundwater in a cost-effective manner.

Optimal Estimation

The problem of optimal estimation was first formally treated in the early 1960s. To solve this problem, it is necessary to obtain best estimates of system variables in dynamic processes described by systems of ordinary differential equations with stochastic (noisy) input terms. In these processes only stochastic measurements can be made. This theory evolved and was applied early in the days of our country's aerospace projects.

The original framework in which the problem was cast dealt with systems of equations that described the dynamics of particles in space. These systems included random wind gusts that acted on masses moving through space at the edge of our atmosphere. Measurements of the motions of these objects consisted only of noise-corrupted radar sitings. Thus, the problem in those terms was to generate best estimates of the positions and velocities of objects acted upon by random forces from data that had intrinsic noise mixed with their signals.

The original solution to this estimation problem appeared in 1961 in the form of Kalman Filter.[28] A wealth of literature followed Kalman's initial work that refined his initial results, provided other solutions to the same problem, and extended the results to apply to general non-linear time-varying systems. Many of these extensions are reported in Gelb,[29] Jazwinski,[30] Schweppe,[31] and in IEEE.[32]

The unique feature of optimal estimation schemes that makes them valuable in designing environmental monitoring systems is their prediction of both the best estimates of system variables and the errors in those estimates. In the estimation algorithms are incorporated deterministic models to compute the mean values of flows, velocities, and concentrations. Also calculated are the variances and covariances in the variables that may be used as measures of error in the estimates. These concepts are shown in Fig. 1. Suppose a groundwater process is acted upon by random forcing terms "v," and further that we are interested in estimating values of the pollutant concentration "p" at some point in the groundwater region. We cannot, however, make perfect measurements of the concentration, and the measurements we do make are corrupted by additive measurement noise "w."

If the estimation algorithms are used, we can generate both the expected values of the concentration "p" conditioned on all past measurement data for the process and the variance "ε," or the error in the expected value. These two variables are shown schematically in Figs. 2a and 2b. The object of the monitoring problem is to determine the fewest number of measurements and the best locations and times to make the measurements that will minimize the total cost of taking measurements while maintaining the error in the pollutant estimates below some allowable maximum value. Suppose the process starts at time t_0. We can allow it to proceed without making any measurements until the error "ε" first reaches its allowable maximum ε_{max}. Suppose the error limit is first reached at time t_1. Then we are required to make some key decisions at time t_1 that will result in making measurements that will minimize the cost of making measurements over the duration of the measurement program. What seems obvious from the sketch in Fig. 2b is that the best positions and number of measurements should be chosen to result in the longest time that the process can drift before another measurement is required; that is, when the error ε next reaches its limit ε_{max} at time t_2. This was one of the immediate results in applying Kalman Filter schemes of optimal estimation to linear time-invariant diffusive transport processes.[33,34]. We anticipate that more complicated optimization schemes will result for the general case of non-linear time-invariant transport phenomena as shown in the postulated algorithm at the bottom of Fig. 1. Finding ways to minimize the cost of a total measurement program for this general case is what the proposed research we describe in this paper is all about.

Extensions of the original concepts of optimal estimation were proposed and to some extent accomplished in the past several years in other areas of systems analysis besides aerospace. Estimation techniques were applied to chemical process modeling, to general mechanical systems, and recently to several studies of the environment. Applications in water quality evolved over the past 10 years. Numerous papers appeared recently in Europe and in the United States. The International Federation for Information Processing (IFIP) hosted a working conference in Belgium in the autumn of 1977 that included several papers dealing with optimal estimation methods applied to environmental problems. After three days of papers presented at that meeting, the indication was that optimal estimation techniques had come of age and matured in the area of environmental studies.[35] The American

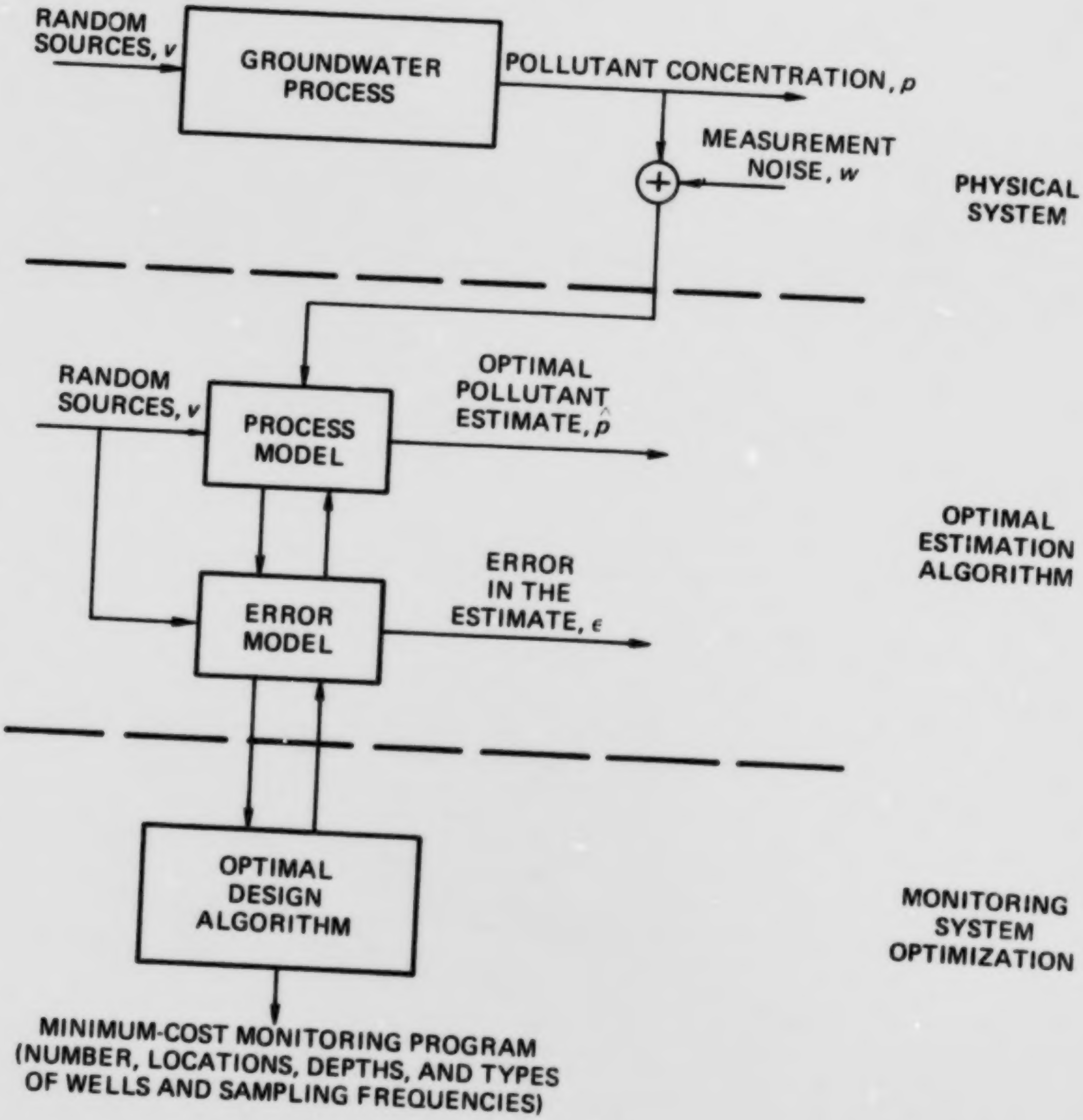
RANDOM SOURCES, v
GROUNDWATER PROCESS
POLLUTANT CONCENTRATION, p
MEASUREMENT NOISE, w
PHYSICAL SYSTEM
RANDOM SOURCES, v
PROCESS MODEL
OPTIMAL POLLUTANT ESTIMATE, $\hat{p}$
ERROR MODEL
ERROR IN THE ESTIMATE, ϵ
OPTIMAL ESTIMATION ALGORITHM
OPTIMAL DESIGN ALGORITHM
MONITORING SYSTEM OPTIMIZATION
MINIMUM-COST MONITORING PROGRAM (NUMBER, LOCATIONS, DEPTHS, AND TYPES OF WELLS AND SAMPLING FREQUENCIES)

Figure 1. Our concept for the optimal design of groundwater monitoring systems includes three major parts: (1) measurements from the actual physical system corrupted with measurement noise; (2) computer-based algorithms that yield optimal estimates of pollutant concentrations and the errors in those estimates; (3) computer-based optimization methods to determine the minimum-cost monitoring program.

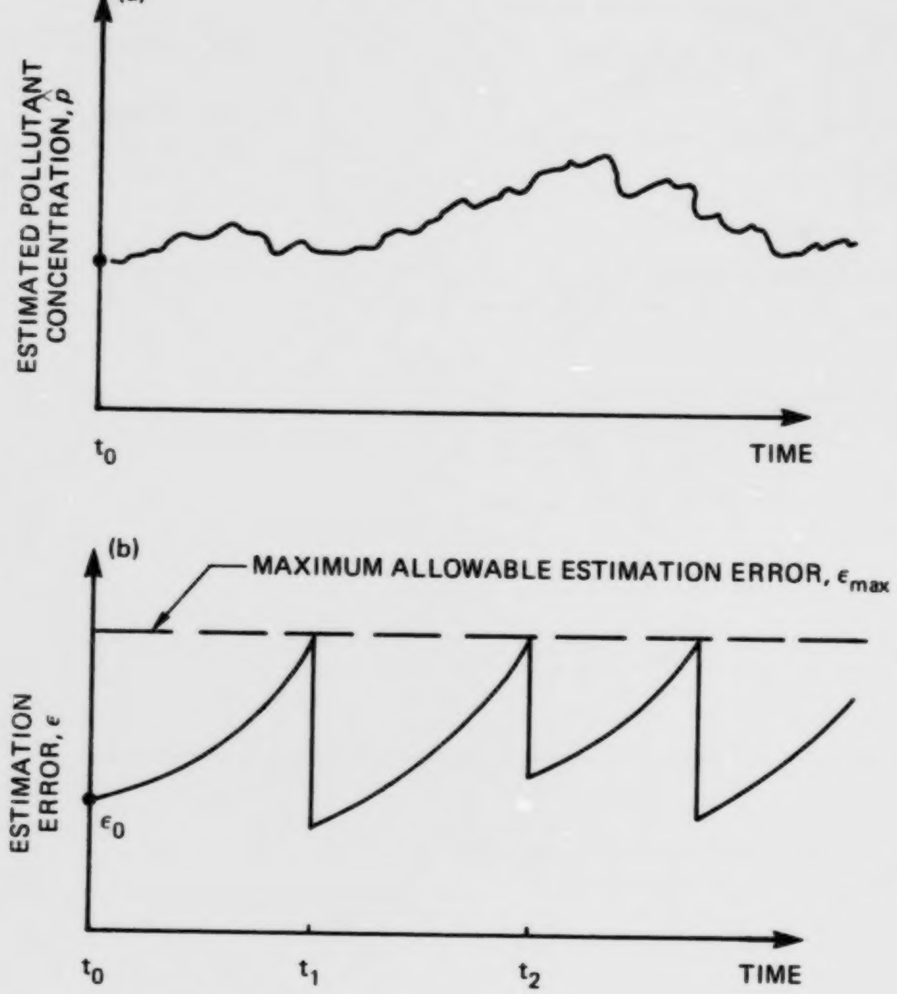

Figure 2. The pollutant estimate (a) and the error in the estimate (b) are indicative of the concept behind our approach to optimal monitoring system design. As the optimal pollutant estimate $\hat{\rho}$ is calculated, the error in the estimate ε is also calculated and used to determine the optimal monitoring program. At the first required sample time t_1, we must choose the best number, locations, depths, and types of samples that will lead to the minimum-cost monitoring program. The best choice results in the longest time between t_1 and t_2, the time of the next required sample.

Geophysical Union recently devoted an entire Chapman Conference to the subject of Kalman Filtering in surface and groundwater hydrology.[36] Included were a wide range of applications of the Kalman Filter technique to problems in rainfall-runoff prediction, stream and lake surface water quality, and groundwater hydrology and quality. In the papers on groundwater applications it was demonstrated that although successful solutions were available for relatively simple problems, solutions for large-scale. real-world applications are still lagging. Reasons for this include insufficient data to adequately support groundwater models, insufficient information on mathematical structure for undergound hydraulic processes, and need for the large dimensionality of the numerical models necessary to adequately characterize complex flow patterns that may occur in groundwater systems. However, the overall impression left after the conference was that the Kalman Filter approach can be a powerful tool in hydrology and, though not well developed at present in groundwater applications, deserves further research in this area to address some of the significant energy development issues that involve our groundwater resources in the future.

Statistical Experimental Design

Experimental design has long been a central tool for the natural and physical scientist. These methods allow isolating effects of the factors in an experiment that yield considerably more information about the structure of response surfaces than is obtained by simply investigating one variable at a time.[37] Federov[38] summarized many of these techniques. Recent work[39] applied many of these ideas to studies of environmental effects of oil spills on intertidal ecosystems. It is clear that the concepts emerging from logical experimental design should affect strategies for minimum-cost measurement of the effects of *in situ* oil shale retorting on groundwater. Key results incorporated in this area will be an important part of our approach.

Optimal Monitoring System Design

Considerable interest has existed over the past 10 years to find optimal methods for designing measurements of dynamic processes. Much of the initial work in this area was generic in nature, applying to mathematical descriptions in the form of systems of first-order, ordinary differential equations.[40] It quickly became evident that many applications of these concepts were needed in the environmental area. Some of the early work centered in the area of optimal siting of air quality sensors.[41] This is such an important problem that members of the EPA Environmental Monitoring and Support Laboratory in Las Vegas hosted a week-long workshop in July 1976. National experts recommended strategies for monitoring criteria pollutants in urban and rural airsheds. The approaches discussed in the working groups were largely heuristic, based on experience of the participants in air quality work. There was an identified need, however, for more research in analytical approaches to the problem of optimal design of air quality monitoring networks.[42]

Much of the early analytical approaches to optimal measurement system design is summarized by Pimentel.[33] Since 1975, other important work includes the paper of Mehra,[43] the work of Seinfeld,[44,45] the continuing interest in the problem by Brewer,[46-49] and the thesis by Henwood.[50] Mehra showed results for optimizing measurement sensor designs and sampling schedules for systems described by models using linear time-varying, ordinary differential equations. Kumar and Seinfeld[44] approached the problem from the outset as one in distributed processes described by partial differential equations. They developed approximate solutions to the design of optimal measurements by using an upper bound to the actual solution of the error covariance matrix. Recently, Koda and Seinfeld, under contract to the EPA, approached the analytical design of minimum-cost monitoring networks for urban airsheds from a design objective point of view.[45] Brewer is delving deeply into the mathematics of the optimization of sensor locations. Recently, one of his students[50] applied Brewer's results to the optimal design of witness well networks to monitor the effects of two-dimensional advective and diffusive transport of a conservative pollutant on an aquifer being affected by a waste leach field.

HOW THIS APPLIES TO OIL SHALE

We believe there is an obvious need for further research in measurement strategies for assessing the effects of in situ oil shale retorting on groundwater resources. It is necessary to fully understand baseline conditions in regional groundwater resources where in situ retorting is slated for development. During development, dewatering of the region being prepared for retorting will alter regional hydrology; flow paths will change, creating areas where flow will be almost at a standstill. During the retorting itself, combustion products will be carried away with the process water; its fate is of concern as it relates to groundwater in the area. After the retorting is complete, the most critical phase of the development cycle begins. As dewatering ceases and native groundwater reenters the area that was retorted, if sufficient environmental controls are not effected, combustion products could leach from the spent shale into groundwater resources and ultimately affect surface water quality.

Thus, we believe the need is clear to develop quantitative, analytical approaches to the rational design of groundwater monitoring systems that will produce the most statistically significant data for the dollar. These cost-effective measurement designs are needed at a variety of different points in the development cycle that have correspondingly different data requirements. The resulting optimal network designs may also be quite different to meet these needs. Optimal monitoring networks to characterize regional groundwater hydrology prior to development may be quite different than those that better apply to making measurements for studying geochemistry. To establish flow relationships, using a large network of small, simple wells may be the best way to make simple measurements of piezometric surfaces; however, for geochemistry and water quality, a sparse network of larger, more sophisticated wells may be required for sampling affected water near developed areas. Measurement programs to study transport and fate may require one type of network to estimate regional hydrology and another to monitor groundwater chemistry. Monitoring systems to meet the compliance requirements of effluent regulations may be of still another best-design depending on the regulations.

SUMMARY

We described our concept of the optimal groundwater monitoring problem. Our proposed methods for solving this problem to apply in the area of *in situ* oil shale retorting have several straightforward steps:

- Source Term Characterization - Ongoing experiments with oil shale processes will make it possible to gather data about combustion products that develop during oil shale retoring, about the leaching of contaminants from spent shale, and about the sorption of contaminants onto aquifer materials. The extrapolated data obtained from simulated *in situ* retorts operated on the surface may yield better numbers than data obtained from actual *in situ* developments, because there is background noise from groundwater intrusion and a lack of process control during underground retorting.

- Hydrological Models - There is a great deal of expertise that exists in numerical simulation of groundwater mass and solute transport. Closed-form analytic solutions exist for linear, time-invariant systems descriptions; sophisticated finite difference and finite element methods can be used for more general cases. We believe that simpler analytical solutions will be more appropriate for applying optimal estimation theory because they are easier to compute and store; this result was true in our survey of models for monitoring system design in the geothermal industry.[20]

- Optimal Estimation - State and parameter techniques estimating stochastic dynamic systems evolved to a high degree of sophistication over the past several years. We have experience with these techniques that includes process monitoring and identification in the nuclear safeguard programs, feasibility studies for use in sophisticated strategic weapons disarmament applications, and initial applications in the area of optimal monitoring system design.

- Statistical Experimental Design - Results from experimental design theory will yield important information to assess designs of an optimal monitoring system. They are a powerful technique to estimate statistical parameters including variance and consistency.

- Optimal Monitoring System Design - Many approaches were made to find minimum-cost designs that measure stochastic dynamic systems. Some of these methods are likely to be powerful techniques for approaching the problem of synthesizing cost-effective groundwater monitoring networks for *in situ* oil shale development activities.

We believe the stage is set for solving real-world problems in this area, and we have familiarity with the above areas of research that will be important in solving groundwater and monitoring problems in oil shale.

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THE DETERMINATION OF FLUORINE IN OIL SHALE RELATED MATRICES USING GRAPHITE FURNACE MOLECULAR ABSORPTION

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The quantitative determination of fluoride in complex sample matrices is difficult because most detection techniques are adversely affected by the presence of interfering species. The widely used ion selective electrode method is not sufficiently reliable and rapid to permit detection of fluoride in geological matrices without prior separation of the analyte. In this paper we describe the adaptation of a rapid separation technique which may be used on complex samples in conjunction with the detection by ion selective electrode or absorption spectrophotometry. The second part of this paper describes the adaptation of electrothermally heated graphite furnace analyzer for the detection of fluoride using an atomic absorption spectrophotometer.

Steam distillation of hydrogen fluoride or hydrogen hexafluorosilicate from acid solution has been widely used, but it is tedious and time consuming. Taves[1] has described a rapid fluoride separation which is both quantitative and easy to adapt to a variety of sample matrices. In this method hexamethyldisiloxane (HMDS) is used to accelerate the diffusion of fluoride by formation of trimethyl fluorosilane (TMFS) which is volatile at room temperature. The TMFS releases its fluoride in aqueous alkaline solution. this method provides a complete separation of fluoride from severe interferences and provides a quantitative transfer of the analyte to a simple interference-free solution. The method also permits preconcentration of dilute samples.

EXPERIMENTAL

One-tenth gram geological solids ground to less than 200 mesh was mixed with 1.0 gram of sodium carbonate-potassium carbonate (1:1 by weight) fusion flux in 25 ml platinum crucibles. The mixtures were fused at 1000°C for 0.5 hours. After cooling 10 ml of 1.0 M hydrochloric acid was added to the fusion mixture to initiate dissolution. The contents were then transferred to a 100 ml plastic specimen cup. A second 10 ml portion of 1.0 M acid was added to the crucible, stirred, and transferred to the plastic cup. A third rinse of 1.0 ml concentrated hydrochloric acid and 4.5 ml of deionized water was sufficient to complete the dissolution and transfer the fusion residue. The sides of the crucible were scraped with a rubber spatula and the contents transferred to the plastic cup with a 4.5 ml deionized water. Some resistant fusions required a fourth rinse consisting of 10 ml of 1.0 M hydrochloric acid. The final solution volume was brought to 50.0 ml using 1.0 M acid.

The fluoride separation was performed in 100 ml specimen cups which have air tight closures. Ten ml aliquots of aqueous standards and acidified samples were pipetted into the specimen cups. A 5 ml plastic microbeaker containing 1.0 ml of 0.1 M sodium carbonate solution was floated on the sample solution. A 0.5 ml aliquot of diffusion reagent (6 M hydrochloric acid saturated with hexamethyldisiloxane, Eastman Kodak Co., Rochester NY) was carefully added to the sample avoiding contact with the carbonate solution in the microbeaker. The diffusion vessel (plastic cup) was immediately sealed and the diffusion process was allowed to proceed for approximately 20 hours. After that period the microbeaker into which the fluoride had diffused was removed and the contents transferred to a plastic container. The solution was then brought to 10.0 ml for subsequent fluoride analysis. At this point any detection technique may be used. Thirty to fifty samples may be conveniently diffused using this method. A schematic diagram of the diffusion apparatus is shown in Figure 1.

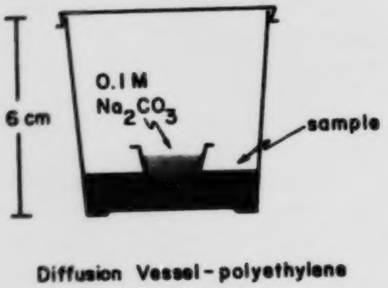

Figure 1. Schematic Diagram Showing 100 mL Diffusion Vessel with 5 mL Microbeaker.

Tsunoda et al.[2] have described a fluoride detection technique which makes use of the formation of gaseous molecular aluminum monofluoride in a graphite furnace. In this technique, AlF is detected and quantified using a conventional atomic absorption spectrophotometer equipped with a continuum U.V. source such as a hydrogen hollow cathode or deuterium arc lamp. We have successfully used this technique on aqueous samples with low concentrations of dissolved species. However, geological fusion digestates and aqueous samples containing high salt concentrations lead to severe interferences. We have adapted the molecular absorption technique for the analysis of complex matrices by first performing the separation described above.

All molecular absorption measurements were performed using a Perkin-Elmer Model 5000 atomic absorption spectrophotometer. The absorption intensities of standards and samples were made using the deuterium background corrector continuum lamp as the sole light source. A wavelength of 227.3 nm and slit width of 0.2 nm band pass was used for all measurements. Peak height measurement with a 10 second window was used to quantify the transient absorption signals. No scale expansion was used. The digital signals were recorded with a PRS-10 digital printer. A Perkin-Elmer graphite furnace (HGA-2100) was used for the formation of the molecular AlF. Sample injections were made using a Perkin-Elmer Model AS-1 atomatic sampler. Twenty µl injections of a 1:1 solution of sample plus reactant solution were used for all determinations. The reactant solution was prepared from the nitrate salts of Al (.01 M), Ni (.005 M) and Sr (.005 M). The injected solutions were dried at 105°C for 40 seconds. Charring occurred over 30 seconds using a logarithmic temperature program between the final drying temperature and a maximum char temperature of 500°C. Atomization (volatization and formation of gaseous AlF) was effected at 2250°C for 7 seconds. A continuous Ar flow at 25-30 ml per minute was used to purge the furnace. Fluoride standards between 0 and 3.0 µg/lm carried though the diffusion separation were used for preparation of the standard working curve. Severe curvature above 5.0 ppm limits the useful detection range of this method.

RESULTS

The detection of fluoride as aluminum monofluoride by molecular absorption in the graphite furnace is adversely affected by the presence of high concentration of most anions and cations. Figure 2 shows the calibration curve of aqueous standards in the absence of any interfering species. Figure 3 shows the percent recovery of 2.0 µ g/ml fluoride when a variety of ions are present at 1000 µg/ml. The extent of signal suppression at these concentrations shows that prior separation of analyte from interferent is necessary in order to ensure accurate analysis. Figure 3 shows the recovery of 2.0 µ g/ml fluoride in the presence of the same interferents after separation by the gaseous diffusion procedure. This procedure yields better than 90% recovery of fluoride for all interfering species except for aluminum and silicate. Figure 4 shows the concentration dependence of fluoride recovery for these two species. Silicate does not significantly interfere below concentration of 500 µg/ml. Quantitative recovery of

TABLE 1. INTERFERENT CONCENTRATIONS IN REPRESENTATIVE SAMPLES

Sample Type	Al	Si
	- - - - - - - - μ g/ml	- - - - - - - - -
Retort--Process Waters		
#A	< 2	13.4
#B	< 2	11.4
#G	< 2	31.4
#O	14.8	10.6
#P	< 2	3.5
Plant Tissue	62.4	37.3
Shale	67.5	57.5
Soil	106 ± 30	84.6
Sediment	80 ± 30	178.0

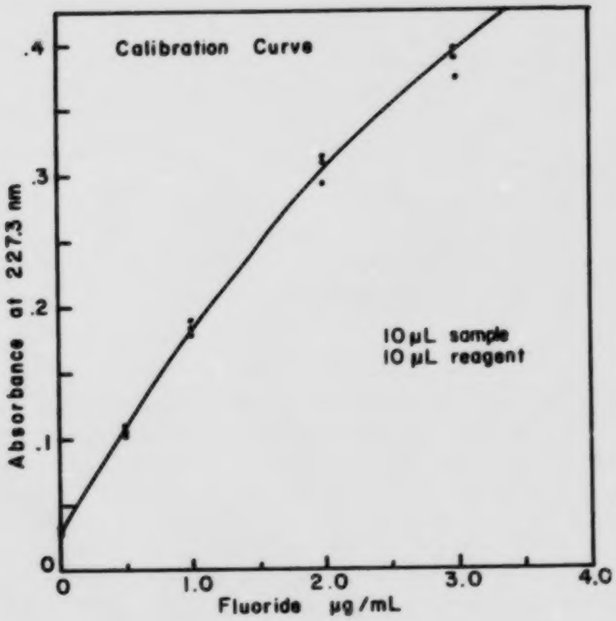

Figure 2. Representative Calibration Curve for Graphite Furnace Detection of Fluoride as Aluminum Monofluoride.

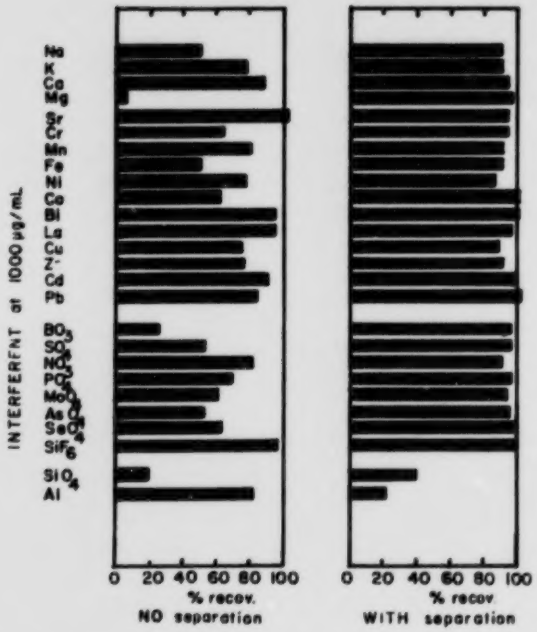

Figure 3. Left: Fluoride recovery obtained by detection of aluminum monofluoride in the presence of selected interferents. Right: Fluoride recovery after gaseous diffusion separation.

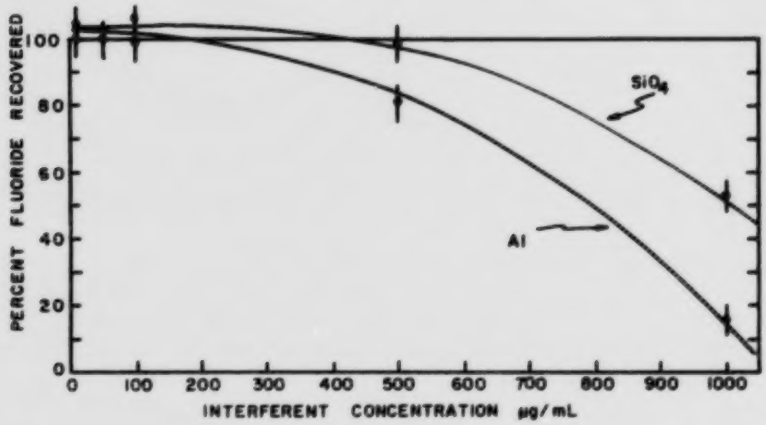

Figure 4. Interferent Concentration Dependence of Fluoride Recovery after Gaseous Diffusion Separation.

fluoride was obtained between 0 and 5 µg/ml. The effect of aluminum is more severe, therefore the concentration of aluminum must be less than 250 µg/ml for quantitative separation of fluoride. These restrictions have not severely affected the application of this method to the matrices encountered in our work. Table 1 shows representative aluminum and silicon concentrations in prepared aqueous solutions of a variety of sample types to which this method has been applied. In all cases, the prepared solutions have silicon and aluminum concentrations below the threshold of significant interference.

In order to estimate the accuracy of this procedure, it is necessary to have standard reference geological samples for which certified fluoride analyses are available. Until these become available we have had to rely upon the samples for which there are published analytical results available. Table 2 shows a comparison of the results obtained using the method described here with published literature values obtained by other methods. The present method has also been applied to plant materials for which the only available, uncertified SRM value has been provided. (NBS Orchard leaves SRM 1571 information only value: 4 µgF/g. This method: 3.8 µgF/g). Other estimates of the accuracy of this method have been performed on surface, ground and drinking waters analyzed by ion selective electrode and colorimetry. Agreement among the analyses was within 10% on more than 50 samples which had concentrations between 0.5 and 6.0 µgF/ml.

TABLE 2. RESULTS OBTAINED ON USGS SOILS

Sample	This Work	Lit. Val.*
	µg/g	µg/g
GxR-1	1280.0	1180.0 ± 190.0
GxR-2	435.0	450.0 ± 180.0
GxR-3	87000.0	79400.0 ± 14600.0
GxR-4	2930.0	2800.0 ± 490.0
GxR-5	290.0	286.0 ± 116.0
GxR-6	290.0	304.0 ± 131.0

* D.M. Hopkins, J. Res. U.S. Geol. Survey, 5, 589 (1977).

We have adopted a simple but effective quality control scheme for detection of systematic errors in routine analyses performed by the technique described here. This two-sample control procedure is based upon the Youden technique developed for interlaboratory tests.[3] The modification used in our laboratory was adapted from the method described by King.[4] We have prepared a composite sample of each sample matrix (plant material, geological, water, etc.). Two aliquots of the appropriate quality control sample labled "A" and "B" are analyzed with each set of unknowns. The sum of the apparent concentrations are plotted after each set of samples have been analyzed. (The concentration is plotted as the ordinate and the

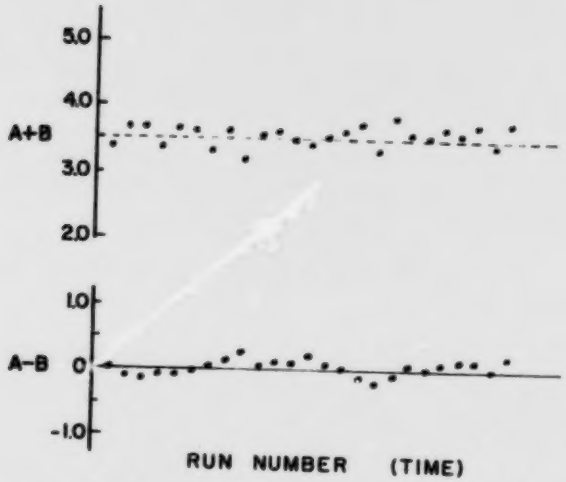

Figure 5. Quality control charts used for detection of systematic and random errors in fluoride method. Abscissa is μ gF/mL in the prepared sample solution.

abscissa is the time order number of the sample set, or analytical number.) By continuously monitoring the plotted results it is possible to detect the onset of systematic errors in the method. The differences between the apparent concentration of aliquot "A" and "B" are also depicted in a time ordered plot. This plot is used to detect random errors in the procedure. Outliers in the sum plot (A+B) are determined using a control limit of ± 2 standard deviations. Similar rejection criteria are used for the rejection of results obtained from analytical runs where the (A-B) plot indicates significant random errors. Figure 5 shows representative results obtained for the aqueous digest of a fused oil shale sample. The relative standard deviation obtained for 25 separate determinations is 4.5%.

CONCLUSIONS

The detection of fluoride by molecular absorption in a graphite furnace can be used successfully on aqueous samples without prior separation when other dissolved species are present at concentrations below 100 μg/ml. Separation by gaseous diffusion should be used for more complex matrices. The detection method described is most useful when coupled with automated sampling techniques. Automated injection of sample into the graphite furnace improves precision and permits large numbers of samples to be analyzed with a minimum of operator attention.

The gaseous diffusion separation described here and by Taves is applicable to a variety of sample types. The quantitative separation of fluoride from potential interferents makes this method particularly useful for preparation of samples prior to other interference-prone detection techniques such as the ion selective electrode and the alizarin complexone spectrophotometric techniques. The techniques described in this paper are currently being applied to oil shale related matrices.

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SAMPLE SIZE REQUIRED FOR ANALYSIS OF OIL SHALE OF WIDELY VARYING GRADE AND PARTICLE SIZE

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ABSTRACT

Almost all the interesting properties of oil shale vary with its kerogen content, which usually shows a wide range of variation in any lot of mine-run shale, sometimes even in a single large block. Even when approved procedures of sampling and subdivision are follwed, misleading analytical results may be obtained if the sample size is inadequate for the range of properties in the lot and the particle sizes involved.

A statistical rationale is developed in this paper that leads to an equation and graphical procedure for finding the minimum representative size of a sample of oil shale. This is applied to several types of analyses commonly done on oil shale. We then look into the case of a retorting experiment in which the oil yield exceeded the Fischer assay.

INTRODUCTION

In a recent report on quality assurance in Federal environmental monitoring[1], ES&T Managing Editor Stan Miller showed how the error variance of any monitoring measurement is the sum of the variances of five major sources of error. This paper is concerned with two of these, the sampling error and the error of the measurement method, as they are involved in assessing chemical and physical characteristics of oil shale rubbles. The special character of mine-run or crushed oil shale, rather different from that of most other minerals, has an important influence on the size of the sample needed to keep sampling error under control.

Minerals are usually prepared for extraction by one or more processes of size reduction, and oil shale is no exception. In many metal ores the metal containing crystals are dispersed in a highly erratic manner amid the gangue. When such ores are crushed, the differing mechanical properties of gangue and metal-bearing minerals, together with the usual high preponderance of gangue, result in particles that are either mostly ore or are essentially all gangue. It is because of this mechanical separation accompanying crushing that floatation methods work so well in ore recovery.

Oil shale, however, is rather differently constituted. Built up at a rate of about 1 millimeter of shale per century, the laminar sedimentation, the inorganic and organic components of what native Americans used to call "the stone that burns" are so intimately bound together that even very small particles can contain some of both components. Still, the percentage of kerogen in Green River oil shale can range, within a few feet of depth in the deposit, from 0 to 30 or higher. Oil shale people like to think in terms of the Fischer assay of the shale, called its "grade," which measures the amount of oil that can be extracted from the shale, in gallons per ton (or liters per Mg). The range for this property is from 0 to about 75 gal/ton (0 to 313 l/Mg), though most of the Green River shale assays at less than 30 gal/ton.

If one picks out a single particle of crushed metal ore, there is a good likelihood that the particle will either contain a high percentage of the metal sought or none at all. For this reason, the rationales proposed for setting the sizes of ore samples have been based on the binomial probability distribution. With this model, in a single trial, one either succeeds or fails. Once the true probability of success is known, or accurately estimated, the distributions of successes and failures in large, randomly chosen samples can be calculated. One can also calculate the standard deviations of the success rates in samples of various sizes, so it is fairly straightforward to set up the size of a random sample needed to make the sampling error as small as one desires. Procedures based on such thinking have been widely used for many years; they are well described in the literature[2] and have more recently been applied to chemical analyses.[3]

A particle of crushed oil shale, though, is unlikely to be either all kerogen or completely free of kerogen; rather it will have some fractional kerogen content more or less close to the true mean content of the lot from which it comes. Some years ago, a 2-inch diameter coring was made through the "Mahogany Zone" (so-called because of its color) near Rifle, Colorado. One hundred fourteen consecutive, 1-foot deep sections of this core, weighing about 3 pounds apiece, were each ground to pass an 8-mesh screen, then subjected to Fischer assay.[4] These samples had grades ranging from 4 to 77 gal/ton (17 to 321 l/Mg). The mean grade was 23.4 and the standard deviation was 14.9 gal/ton*. The picture was very similar for 86 consecutive specimens taken from a second core drilled in another county of Colorado. Because each core was targeted on the Mahogany Zone, neither sample can be considered wholly random, though hundreds of other cores from the Green River Basin show that these two are fairly typical.

Another property measured on the powders made from these cores[4] was the specific gravity (relative to water at 60°F) and, as expected, the grade of the shale decreases steadily, though not linearly, as the specific gravity increases. For specific gravity, the mean of the 114 samples was 2.266 while the standard deviation was 0.220*.

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* These values were not given by Smith[4] but were calculated by me from point coordinates read off Smith's Figure 1.

CHOOSING A SAMPLE SIZE

Suppose now that we must sample some broken shale and estimate the value of some property like grade or density. The problems connected with actually collecting the sample are dealt with in handbooks[1] and in the ASTM procedure for sampling coal,[5] and I shall not dewll on the mechanics of assuring randomness but shall assume that, whatever the size, randomness can be achieved. "Randomness" means, simply, that each of the particles of the lot has the same chance of being chosen for the sample. It should be apparent that if only one particle were taken, its grade might be anything between 5 and 70 gal/ton. However, if our sample consisted of 10 randomly chosen particles of about the same size, the mean grade of the 10 would have a standard error of $\sigma/\sqrt{10}$, where σ = the standard deviation of grade in the lot. If we selected n particles, the sampling error of the mean grade (or property of interest) would be $\sigma/\sqrt{n}$. However, this is only the sampling error. Even if we could reduce this error component to zero, the error of measurement would still be present. Actually, since the two are independent, their squares, the sampling and measurement variances, are additive. The variance of the estimated mean is given by--

$$\sigma_{\bar{x}}^2 = \sigma_s^2 + \sigma_m^2/r = \sigma^2/n + \sigma_m^2/r \qquad (1)$$

where σ_s^2 = the sampling variance;

σ_m^2 = the variance of the measurement method (one determination);

r = the number of determinations made.

Equation 1 is valid no matter what the form of the distribution of the property of interest in the lot. Since the standard error of the estimated mean $\sigma_{\bar{x}}$ cannot be smaller than the larger of its two constituent errors and will not be reduced appreciably by making the smaller one still smaller. It is shown in the Appendix that, if the costs of sampling and measurement are known, there is an optimal choice of r and n that minimizes the cost of obtaining any desired $\sigma_{\bar{x}}$. In the absence of such cost data, a reasonable rule of thumb is to let the two variance components be equal. The final combined error of the estimate will then be σ_m times $\sqrt{2/r}$, which will usually be acceptable. If that equality is solved for sample size we get--

$$n = r(\sigma/\sigma_m)^2 \qquad (2)$$

An interesting property on which to try this equation is density. The standard deviation for single determinations of density on finely ground shale by helium pycnometry is about 0.005 g/cm³. If the practice were to determine density for three samples of the powder, then r would be 3. Taking the value of σ equal to that calculated from Smith's data, 0.220 g/cm³ and applying Eq. 2, we find the sample size to be $n = 3(0.220/0.005)^2 = 5800$ particles.

Now, we don't really want to count out these particles, especially when they are very small. To what mass of particles in a given narrow size class does this number correspond? Particle mass in grams is given by the equation

$$M = f\, d^3\, \rho \qquad \text{for a single particle and by} \tag{3a}$$
$$M = n\, f\, d^3\, \rho \qquad \text{for n particles} \tag{3b}$$

in which d = the "size" of the particle, cm;
ρ = the density of the material, g/cm^3;
f = the volume shape factor.

It is generally accepted that screening measures the second largest principal dimension; this is the dimension we call "size." The shape factor f would be unity if the particles wer cubes or /6 if they were spheres, but for our shale particles, which vary from near-cubes to thin flakes, f exhibits considerable variation. For 10 particles taken from our "masterbatch" material, which passes a 1-inch (2.54 cm) screen but remains on a half-inch (1.27 cm) screen, d ranged from 1.250 cm to 2.620 cm, averaging 1.890 cm, while f, calculated from Equation 3a, ranged from 0.148 to 0.397, averaging 0.284. For particles like these, Eq. 3a gives $M = 0.284 \times 1.890^3 \times 2.209 = 4.24$ g. This compares rather well with the measured average mass of 4.68 g, considering the small size of the sample and the large variations in d and f. The "masterbatch" was created by crushing, thoroughly blending and screening larger material from all parts of our shale pile and may be expected to contain the whole range of density of our pile of Anvil Points shale. For these particles, then, the total mass of a random sample would be $M = 5800 \times 4.24 = 24{,}600$ g.

In dealing with a specific size fraction, specified by the openings of screens retaining and passing all of the sample, there is a question as to what average size should be used to represent the fraction. If the two screen openings defining the fraction differ by no more than a factor of 2, the arithmetic average opening may be used for the mean size with an error in $(\bar{d})^3$ of less than 10 percent (low). That is

$$\bar{d} \cong 0.5\,(d_1 + d_2) \tag{4}$$

By combining equations 2, 3b and the concept of mean size, we get the final equation for the sample mass in grams.

$$M = f\, \sigma\, r\, (\sigma/\sigma_m)^2 (\bar{d})^3 \tag{5}$$

For density estimation, and assigning conservatively high values of 0.4 to f and 2.5 to and assuming r = 2, Eq. 5 reduces to

$$M = 3870\, (\bar{d})^3 \tag{6}$$

This equation is plotted in Figure 1 with some familiar screen fractions indicated.

For some very precise determinations, for which σ_m is very small, setting the sampling variance σ^2/n equal to the measurement variance σ_m^2/r

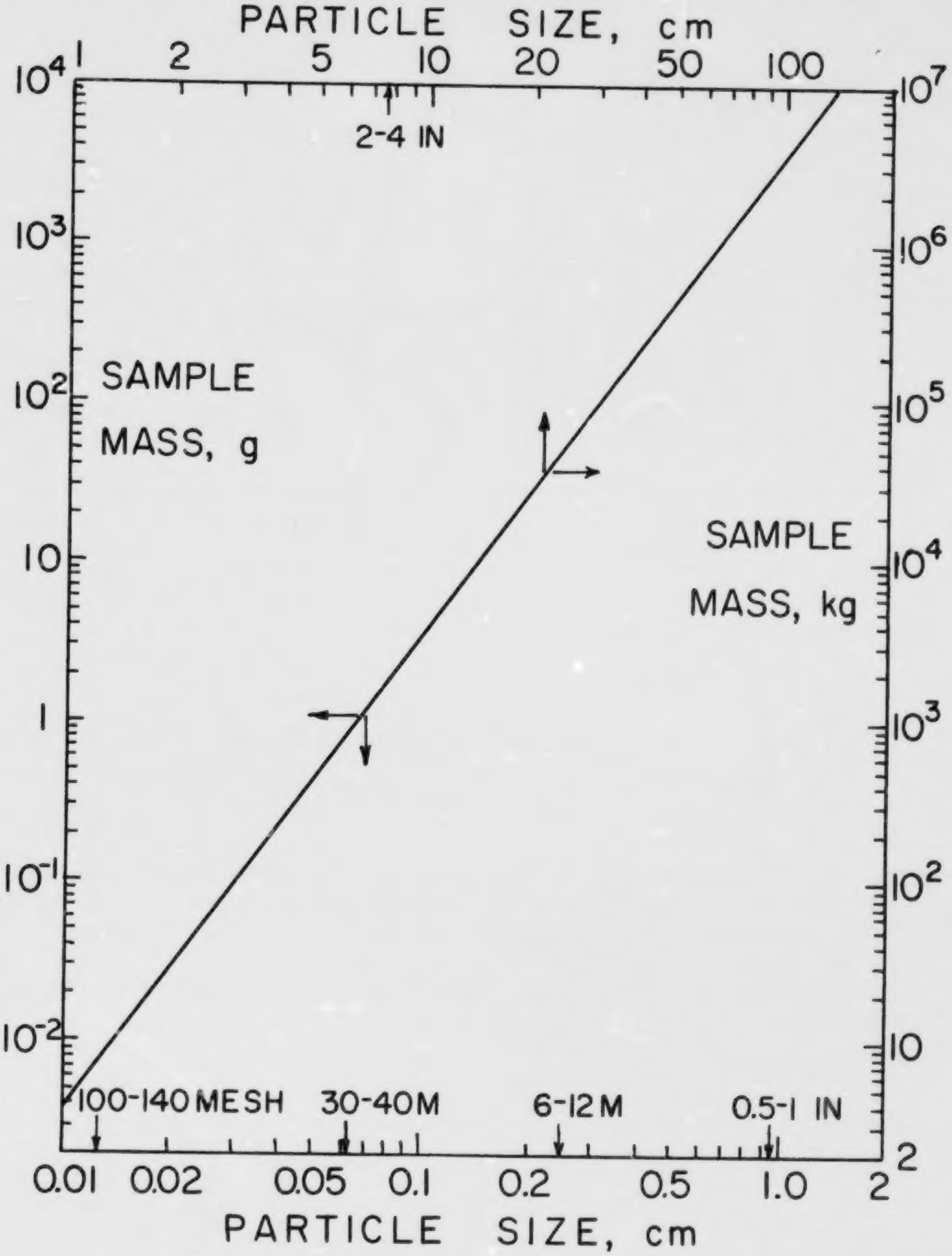

Figure 1. Plot showing dependence of sample size required on size of particles for measurement of density in oil shale by helium pycnometry (two determinations).

may provide an error of estimate, $\sigma_{\bar{x}}$, that is much smaller than is necessary for the use that is to be made of the estimated mean. One can instead choose a larger $\sigma_{\bar{x}}$ that will effectively be equal to $\sigma/\sqrt{n}$. Then the sample size n would be given by $n = (\sigma/\sigma_{\bar{x}})^2$ and, since repeating the measurement would not improve precision, r would be 1. This variance ratio, and $r = 1$, can be substituted for $(\sigma/\sigma_m)^2$ and r in Eq. 5 and its derivatives.

I chose density as the illustrative property in this development not only because it is a property of interest but because many chemical and physical properties of oil shale are directly or inversely related to density. Grade, kerogen content, organic-carbon content and heat capacity, for example, are inversely related while mineral content and strength properties are directly related. However, some properties vary more than density or may be measured with more or less precision than density and, as Eq. 5 tells us, these characteristics are strong determinants of sample size. What minimum size sample should be taken for the determination of grade, the property of greatest interest?

From the results of a roundrobin test program undertaken a couple of years ago,[6] I calculated the measurement error from duplicate determinations for the nine laboratories using the USBM method to be 0.371 gal/ton (with degrees of freedom $\nu = 216$). With the value of 14.9 gal/ton calculated from Smith's data[4] for σ and the same values for f, r and σ as for density, Eq. 5 condenses to

$$M = 3220\ (\bar{d})^3 \tag{7}$$

Organic carbon content of shale is proportional to grade[7] and is given approximately by the equation.

$$OC = 0.467\ G \tag{8}$$

Where OC is in weight percent of raw shale weight and G in gal/ton. For the region sampled by Smith, then, σ for organic carbon would be 0.467 x 14.9 = 6.96 wt %. From many sets of organic-carbon analyses made on samples of oil shale in our Chemistry Department, I have estimated σ_m for this determination to be 0.063%C (υ=)50. Again applying Eq. 5 with the same values of f, r and ρ we get

$$M = 24{,}400\ (\bar{d})^3 \tag{9}$$

The much larger sample size required here is mostly a consequence of the greater precision of the organic-carbon determination and our initial decision to equalize the error contributions of sampling and analysis. If an estimation error comparable, percentagewise, to that for density or grade is acceptable for organic carbon, then the sample size required for density will suffice for organic carbon, too.

Equation 5 differs from sample-sizing methods offered elsewhere mainly in its dependence on the third power of the particle size rather than the second (or lower) power, and in the introduction of the standard deviations of the continuously distributed property being estimated and the method of measurement. Except for relatively large particles, about 10 cm and larger, Eq. 5 tends to give sample sizes smaller than those prescribed in references 2 and 3. Figure 2 is a concurrency chart that solves Eq. 5, taking $f\rho = 1$, from inputs d, r and σ/σ_m.

PARTICLES WITH A WIDE RANGE OF SIZES

The foregoing treatment has dealt with particles of a single size or, at least, with a narrow size range. Mixing and crushing operations always yield particles with size distributions spanning one or more orders of magnitude, and it may not be practical (or even advisable).[8]

Consider how sampling-error variance is made up when there are only two distinct sizes. In general the property to be measured will either consume the whole sample, or it will be subjected to further size reduction and splitting. For simplicity, consider the first case. The sample will consist of a mass fraction, m_2, of the smaller size and remainder, m_2, of the larger size. Suppose the average value of the property of interest, say grade, in each of the size fractions is G_1 for the smaller-size material, G_2 for the larger. The average for the entire batch will be $G = m_1G_1 + m_2G_2$. By Eq. 1, the variance of G_1 will be σ^2/n_1 while that of G_2 will be σ^2/n_2. We assume that the mass fractions in the sample can be measured with errors that are negligible in comparison with the variations in the G_i, a very sound assumption with modern weighing equipment of industrial grade or finer. Since the grades of all the particles are independent of each other, we can apply the principle of additivity of variance again, just as we did in Eq. 1. The result is

$$\sigma_G^2 = m_1^2\ \sigma_{G_1}^2 + m_2^2\ \sigma_{G_2}^2 = \sigma^2[(m_1^2/n_1) = (m_2^2/n_2)] \tag{10}$$

By Eq. 3b, $n_i = M_i/f\rho d_i^3 = m_iM/f\rho d_i^3$. Substituting into Eq. 10, we get

$$\sigma_G^2 = (\ {}^2f\ /M)[m_1d_1^3 + m_2d_2^3] \tag{11}$$

By the same line of reasoning, the sampling variance in $\bar{G}$ when there are k discrete size classes will be

$$\sigma_G^2 = (\sigma^2 f\rho/M) \sum_{i=1}^{k} m_id_i^3 \tag{12}$$

Since density varies along with other properties of oil shale, we could make this equation a little more precise by subscripting density and summing the product $_im_is_i^3$. However, we are merely trying to arrive at a satisfactory sample size so a single highest value of density, whose percentagewise variation is rather small anyway, will give a sample size only a little larger than the necessary minimum.

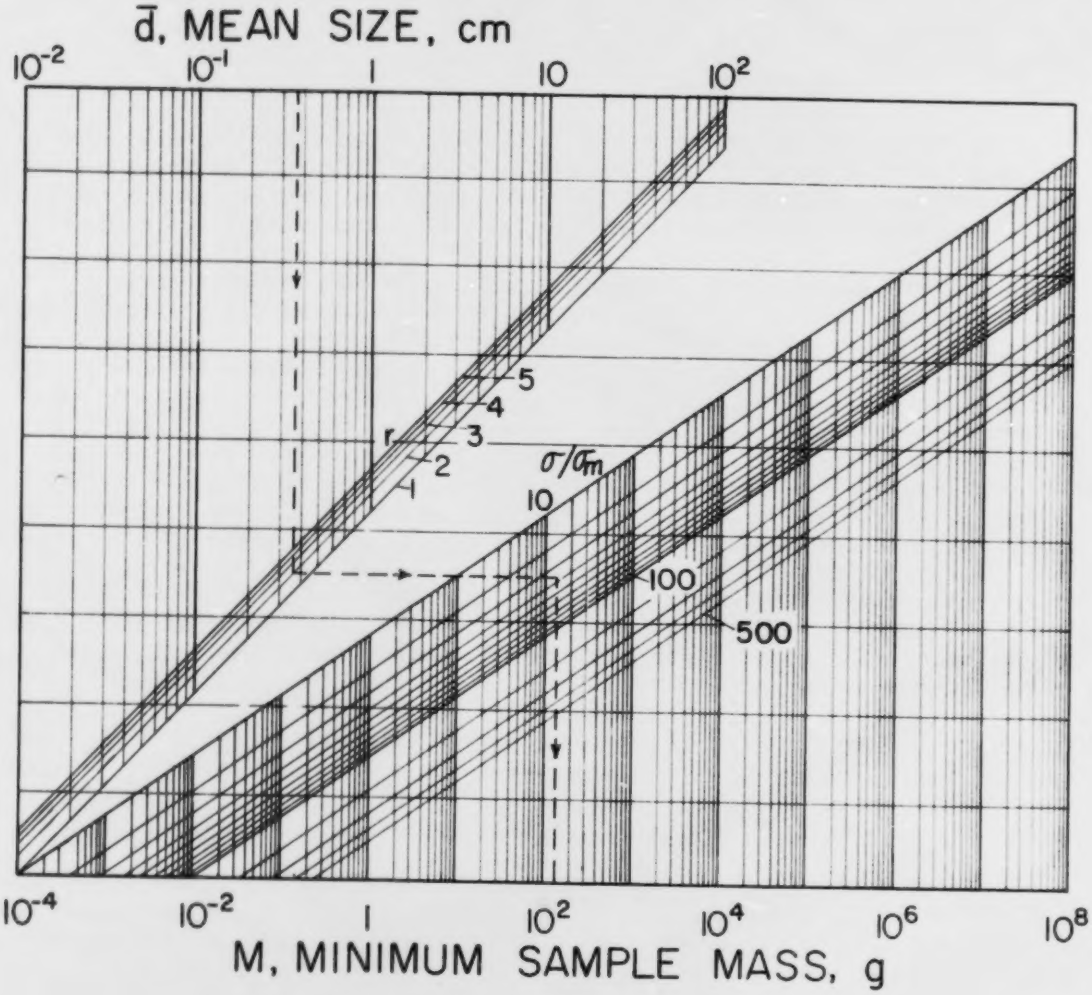

Figure 2. Concurrency diagram that solves Equation 5, giving sample size required for tests on oil shale particles. Enter at top with particle size or mean size for fraction or distribution, drop down to r, number of replicate measurements to be made of property, then move horizontally to appropriate value of σ/σ_m, then downward again to read mass of sample. Example (dashed lines) for d = 0.36 cm, r = 2 and σ/σ_m = 38 gives M = 135 grams.

If particle size is continuously variable with a mass-based probability density m(d), the analogous equation to Eq. 12 is

$$\sigma_G^2 = (\sigma^2 f\rho/M) \int_{d_{min}}^{d_{max}} d^3 m(d)\, dd \tag{13}$$

We have found that size distributions for crushed oil shale are approximately lognormal, as is the only well-documented size distribution for mine run shale that I know of.[9] This property is easliy tested by plotting (when such data are available) the cumulative weight percent passing a series of graded screens versus the screen size on lognormal probability graph paper. If the distribution is lognormal the plot will be a straight line. If m(d) in Eq. 13 is the lognormal density the integral of Eq. 13 can be evaluated with the aid of tables of the cumulative normal distribution. On the other hand, if the screening data is available, we can work with Eq. 12, letting d_i for each fraction equal the arithmetic mean of its two screen sizes.

Let us now define the mean size for a distributed sample as that single size which, taking the sample as a whole, makes the sampling variance $\sigma_G^2 = \sigma^2/n$. By Eq. 3b, $n = M/f\rho(\bar{d})^3$, where $\bar{d}$ is the required average diameter. Thus, $\sigma_G^2 = (\sigma^2 f\rho/M)(\bar{d})^3$. Comparing this with Eq. 12, it is clear that the required average diameter must be

$$\bar{d} = (\Sigma m_i d_i^3)^{1/3} \tag{14}$$

It is worth reflecting on the structure of this average for a moment. In crushed shale, the larger size particles tend to be present in larger amounts, so the average diameter for sampling-variance purposes will tend to be close to the high end of the size range. If that range is considerable, say 10 to 1 or more, the smaller sizes will have almost no influence on the average size. If no screening data is available from which to compute $\bar{d}$, a safe size is the largest size visible in the mass being sampled.

Let's recap the sample-sizing procedure. First, one uses the known or estimated standard deviation of the property to be tested, together with the measurement error and the number of repeat determinations to set the number of particles needed. Then, using the appropriate mean particle size, Eq. 4 for narrow size fractions, Eq. 14 for multiple discrete sizes or wider size distribution, and taking the fρ product = 1, the required mass of sample is found from Eqs. 3 (or 5), or Figure 2.

A CASE OF TOO-PLENTEOUS YIELD

The core of our oil shale program at LLL is the experimental simulation of modified *in situ* retorting with two specially constructed aboveground retorts. Each of these retorts is equipped with an elaborate, multistage collection system that recovers all the oil that leaves the retort as liquid, mist and vapor. For each run, the yield, expressed as a percentage of Fischer assay, is found from the equation

Y = 100R/MG
R = the gallons of oil recovered,
M = the mass of oil shale loaded into the retort,
G = the grade of the shale, as determined by two Fischer assay samples of the shale loaded.

In a dozen or so combustion runs made in our smaller retort over the past two years we have obtained yields averaging 91.5%. Some oil is lost during retorting by combustion, coking and cracking that is not lost during the Fischer assay. The quantities R and M are measured with sufficient accuracy that their errors are negligible in comparison with that of the assay. If we take for that error the value given earlier, 0.371 gal/ton, the mean of two determinations will have a standard error of $0.371/\sqrt{2} = 0.262$, so a 95% confidence interval for the true grade should be that mean ± 0.53 gal/ton, approximately. Since this amounted to 2.2% of the assay itself, we had been allowing in our thinking for about this much error in the yield. We were therefore surprised when our yield for Run S-18 of the small retort turned out to be over 103%.

Well, as you no doubt have noticed by now, we failed to allow for the introduction of sampling error. We had been careful to assure that our sample was representative of the load and did not realize that, because of the relatively large size of the particules that make up most of the sample mass, our sample--38.2 lb--was too small.

When I began to suspect this cause, I looked for some data from which I could estimate the standard deviation of grade in our shale pile. In the summer of 1977 we loaded our large retort with a matrix of shale crushed to less than 3 inches in size in which were embedded 68 larger blocks that were selected from our pile. We began by picking blocks in a narrow size class, 8 to 12 inches, from all over the pile until we had 105 blocks. Except for their size, they were a random sample of our stock. Each of these was weighed in the air and weighed again under water to determine its density, then the block densities were adjusted slightly to correct for small amounts of included voids. From the corrected density, the average grade of each block was estimated using a slightly revised equation based on the data of Smith.[4] The mean and standard deviation were 25.3 and 10.05 gal/ton; our shale pile is a little richer and is not quite as variable as the specimens of Smith.

The material loaded in Run S-18 was obtained representatively from our entire shale pile by a large scale crushing and sampling procedure, which we call "donkey-walking." This procedure, whose details I'll skip, apportions the material being crushed evenly, a little at a time, to a circle of many 55-gallon drums. Subsequent examination of such drums has shown that they are very closely alike in their size distributions and average chemical properties. The S-18 load came from one such drum, which was first similarly redistributed, now on a much smaller scale, to 5-gallon buckets. The buckets were loaded completely into the retort until it was full and all the leftover material was screened, then repeatedly recrushed and redistributed

TABLE 1.

Screen Fraction, Inches or Mesh nbr	Mass, lb.	Arithmetic Mean Size, cm	Estimated Number of Particles
-3, + 2 in	11.8	6.35	33
-2, + 1	10.6	3.81	139
-1, + 1/2	5.7	1.90	600
-1/2, + 1/4	4.0	0.96	3300
-1/4, + 6 mesh	1.7	0.488	10600
-6, + 12	1.5	0.252	68000
-12, + 20	1.1	0.126	360000
-20	1.8	< 0.05	> 10^7

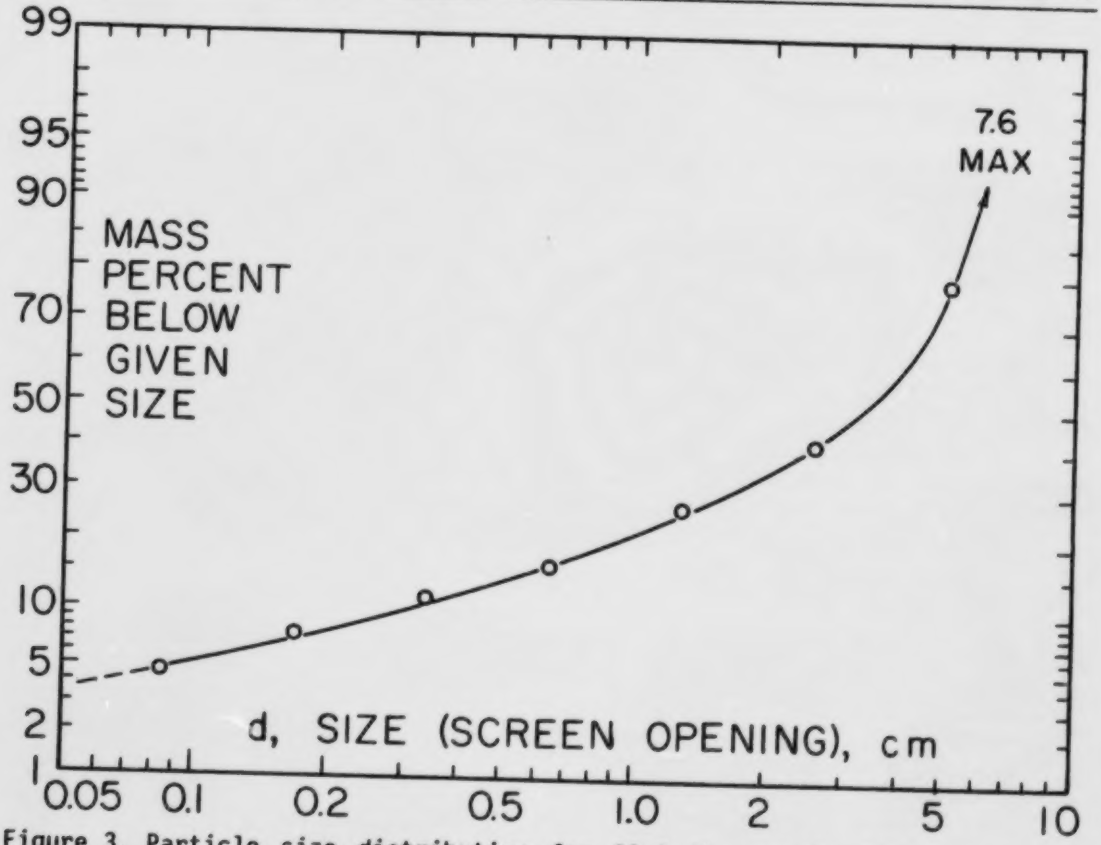

Figure 3. Particle size distribution for 38.2 lb. sample left over from load for Run S-18. While lower region is fairly straight, sharp upward curve at right end indicates severe truncation of theoretically long right tail of lognormal probability distribution.

into smaller quantities to get the 100-gram, finely-divided samples required for the Fischer assay. The size distribution of the leftover 38.2 pounds of material is given in Table 1, along with the number of particles in each screan fraction as estimated from Eq. 3b with $f = 0.284$ and $\rho = 2.2$ g/cm^3. The cumulative mass-based size distribution is also plotted in Figure 3 on lognormal probability paper.

From the table it is clear that, although there are plenty of particles in the size classes below 0.5 inch, there are probably too few in the three upper classes that constitute 73.6% of the sample mass, with the top two sizes being very severely underrepresented. The average size for this sample, calculated by Eq. 14, is 4.65 cm; by Eq. 5, the sample mass required to at least equalize sampling and measurement contributions to the error of the estimated grade is $M = 1 \times 2\ (10.05/0.371)^2\ (4.65)^3 = 148000$ g = 325 lb. With only 38.2 lb, our sampling error drowns the measurement error and makes the combined error of the estimated grade equal to 0.66 gal/ton. This figure corresponds to a 95% confidence band for yield in Run S-18 of more than ± 5%, so our true yield in that run was probably what it should have been, something under 100 percent.

CONCLUSION

I have provided equations for choosing a minimum adequate sample size from a reservoir of oil shale rubble, based on the fact that properties of oil shale are continuously and intimately, rather than discretely, distributed throughout all the particles. The guiding principle is that the contributions of sampling and measurement errors to the total error of estimation shall be equal. Where accurate costs of sampling and measurement are known, that principle may be discarded and a minimum-cost sample size can be determined for any desired estimation error. The sample size is proportional to the third power of the particle size; when the reservoir contains distributed sizes, the mean sample size to be used in determining sample mass is dominated by the larger sizes present. Neglecting the contribution of error due to sample size, even when procedures are followed to make the sample representative, can cause serious underestimation of errors in estimated properties of quantities derived from them.

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APPENDIX

Suppose it is desired to estimate some property, x, of a reservoir of rubbled oil shale and that information is available on the costs (1) of collecting and preparing the sample for the measurement and (2) of making the measurement on the sample. Also known are the variances σ^2 and σ^2 of the property in the reservoir and the measurement, respectvely. It is not unreasonable to assume the cost of sampling to be proportional to the sample size (either M or n, since, by Eq. 3b they are proportional) and the cost of the determiantion to be proportional to the number of replicates run. Then we can write

$$C = c_s n + c_m r \tag{A1}$$

How should n and r be chosen so as to achieve a certain estimation error, $\sigma_{\bar{x}}$, at the lowest cost?

Equation 1 gives the variance of the estimate.

$$\sigma_x^2 = \sigma^2/n + \sigma_m^2/r \tag{1}$$

$$r = \sigma_m^2/(\sigma_x^2 - \sigma^2/n) \tag{2}$$

Substituting into Equation A1,

$$C = c_s n + C_m \sigma_m^2 \, (\sigma_x^2 - \sigma^2 1n)^{-1} \tag{A2}$$

$$\frac{dC}{dn} = c_s + d_m \sigma_m^2 \, (-1)(\sigma_x^2 - \sigma^2/n)^{-2} \, (-)\sigma^2(-)(1/n^2)$$

$$= c_s + c_m \sigma_m^2 \sigma^2/(n\sigma_x^2 - \sigma^2)^2 \tag{A3}$$

Set dC/dn = 0, solve for n.

$$n = (\sigma^2/\sigma_{\bar{x}}^2) \quad \times \quad \left[\sqrt{c_m \sigma_m^2/c_s \sigma^2} + 1 \right] \tag{A4}$$

Now taking the second derivative,

$$\frac{d^2C}{dn^2} \quad = 2\sigma_x^2 \sigma_m^2 \sigma^2 c_m/(n\sigma_x^2 - \sigma^2)^3 \tag{A5}$$

Since $\sigma^2_{\bar{x}} > \sigma^2/n$ by its definition, $(n\sigma_x^2 - \sigma^2)^3$ will be positive for all $n \geq 1$. Therefore, d^2C/dn^2 is positive for n as given by Eq. A4, so that n does define the minimum for C.

If that n is now substituted into Eq. 1b, one obtains after some manipulation

$$r = (\sigma_m^2 / \sigma_x^2) \left[(1 + \sqrt{c_m\sigma_m^2 / c_s\sigma^2}) \Big/ \sqrt{c_m\sigma_m^2 / c_s\sigma^2} \right] \qquad \text{(A6)}$$

Dividing this into A4, we find that the ratio of n to r is given by

$$n/r = \sqrt{c_m\sigma^2/c_s\sigma_m^2} \qquad \text{(A7)}$$

Example of use:

Suppose for estimation of grade you wanted $\sigma\bar{G} = 0.5$ gal/ton. Sampling and preparation (repeated grinding, splitting, screening) costs for the environment involved are proportional to the mass of sample taken, about \$2 per pound for samples of 20 lb and more. Mean size is about 5 cm. Taking $f\rho = 1$, $c_s = \$2 \times f\rho(\bar{d})^3/(454\ \text{g/lb}) = 56¢$/particle. c_m = \$10 per assay, $\sigma^2 = 10^2$, $\sigma_m^2 = 0.371^2 = 0.1376$. Equation A4 gives n = 463 pieces or 127 lb, and r is found to be 4 from Eq. A6 or A7.

SAMPLING AND HANDLING OF
OIL SHALE SOLIDS AND LIQUIDS

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INTRODUCTION

This paper is a practical review of what various groups have learned while sampling, handling, and preserving materials from oil shale retorting operations. The experience of this group has been in the preparation of raw and retorted shale from the TOSCO II process,[1] the Fischer assay of a standard shale,[2] [3] and the sampling and analysis of raw and retorted shales, oils and waters from the Paraho process.[4] [5] [6] Most of these studies concern surface rather than in situ retorts. However, the observations of other research groups which have been sampling oil shale materials related to in situ retorting have been considered in the writing of this paper. The experiences of the Berkeley group[7] [8] and the Battelle group[9] have been especially useful. The methods of analysis that have been used in this study are not discussed in this paper but can be found in other reports.[3] [5] [6] [10] [11] There has been much written on the sampling, handling, and storage of environmental materials; obviously the methods suggested here have been based on that accumulated wisdom. In this regard, a recent review by Maienthal and Becker[12] provides a good summary of the procedures used for sampling and handling environmental materials. Most of the various procedures used here are mentioned in that review.[12]

Regarding the Quality Assurance Program of the Environmental Protection Agency, this paper will be more applicable to the questions of siting criteria, field methods, sampling frequency, and preservation of samples.[13] The questions of data acquisition, standard methods of analysis, equivalent methods of analysis, reference samples and monitoring capabilities are not discussed here.

The paper is divided into two main sections: SAMPLING and HANDLING AND PRESERVATION. Within each section there are subsections on solids and liquids, and each subsection is divided into conclusions, discussion, and recommended procedures.

SAMPLING

Solid Materials

Conclusions -

1. Sampling raw and retorted shale every half hour using the sampling systems on the Paraho retort places a burden on the sampling system, the retort personnel, and the laboratory personnel. Fortunately, conclusion 2 states that sampling this often is not necessary.

2. The results of the sampling program for the Paraho retort suggest that taking a weekly composite sample is sufficient for monitoring the inorganic constituents in raw and retorted shale. The organic constituents can be monitored by taking a daily composite sample.

Discussion on the Conclusions -

The conclusions on sampling are primarily the result of the sampling program undertaken at Paraho in the summer of 1977. This was one of the more extensive sampling studies ever attempted on an oil shale retort. The details of the program and the initial results have been published in other reports.[4] [5] [6] A summary of the research follows.

The Paraho retort is an aboveground, vertical kiln which processes oil shale as a physically heterogeneous feedstock. The shale is crushed to -3 inch to +1/2 inch normal size. A study was made to determine how the trace elements varied in the retort. A nested sampling scheme was devised which went for 30 days to test the variation in the daily, the 8-hour, the 1-hour and the analysis levels. A diagram of the sampling design is shown in Figure 1. The sampling of the other materials at Paraho was fit to the sampling of the raw shale. For the retorted shale, the same design (Figure 1) as for the raw shale was used.

One other goal of the Paraho program is to try to uncover element relations between the feedstock and the products. Thus, the timing of the collection of the various materials has to be considered. It takes about 4 hours for feedstock to pass through the retort and exit as retorted shale. Paraho measures the amount of oil collected in a day from 0000 to 2400 hours. Thus the retort day starts at 2200 of the previous day for the raw shale, at 0000 for the product oil nad water and at 0200 for the retorted shale. On this time scheme, the raw shale, retorted shale, oil and water are related to one another. Figure 2 is a diagram of when samples were collected on a typical retort day.

The system used for sampling raw and retorted shale at the Paraho retort has been previously described.[4] However, there are some important features of the system, that require mention in this paper. At preset intervals of usually 30-60 minutes, a motorized gate diverts the complete

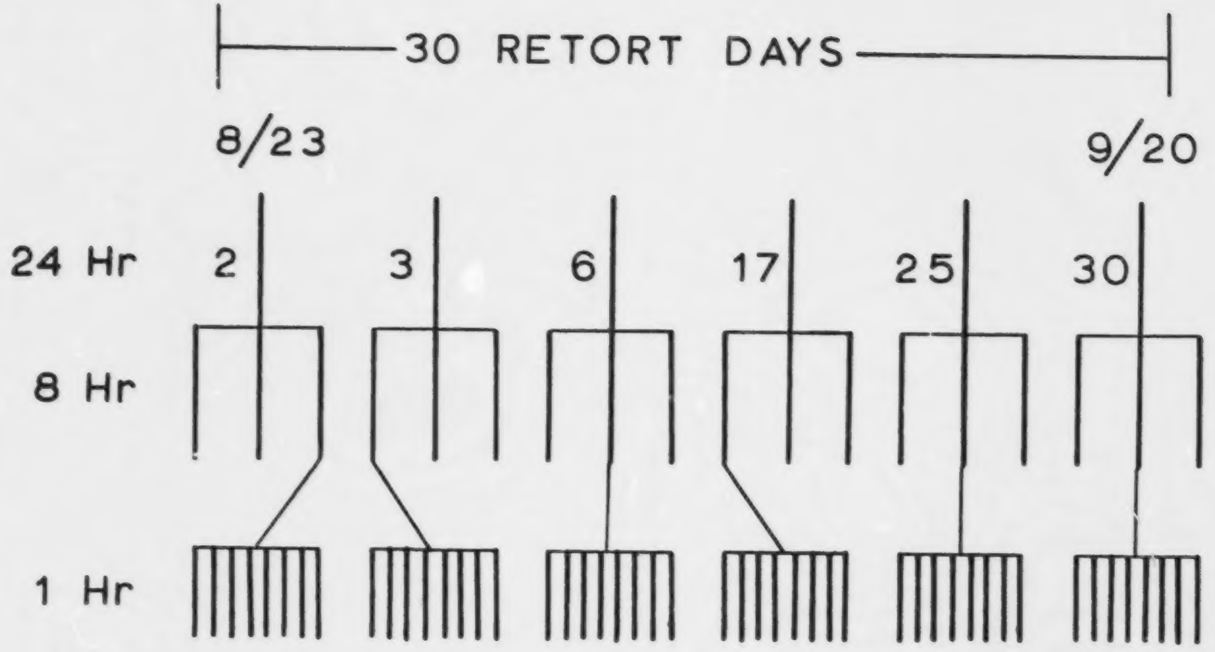

FIGURE 1. TIME NESTED PARAHO SAMPLING DESIGN.

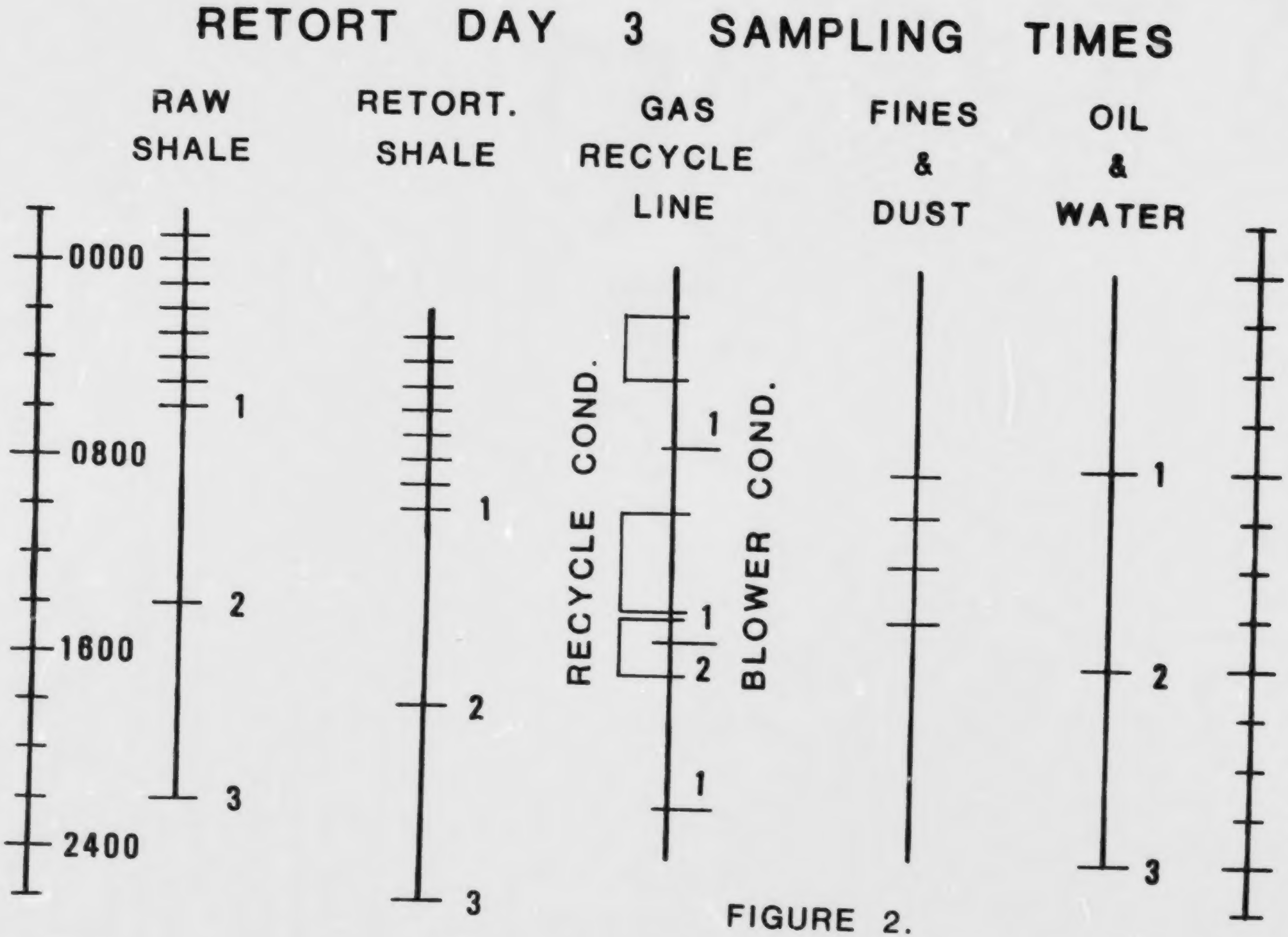
RETORT DAY 3 SAMPLING TIMES
RAW SHALE
RETORT. SHALE
GAS RECYCLE LINE
FINES & DUST
OIL & WATER
0000
0800
1600
2400
1
2
3
1
2
3
RECYCLE COND.
BLOWER COND.
1
1
2
1
1
2
3

FIGURE 2.

flow on the conveyor belt to the sampler. This amounts to around 200 pounds of material in a single cut. The sample passes through a series of crushers and splitters until a representative two pound sample is retained. The hourly samples can be taken or they can be accumulated to make an 8-hour or 24-hour composite sample.

The results of the analyses on the raw shale are shown in Table 1. The oil, water and gas analysis is by Fischer assay[14] and the elemental analyses are by energy dispersive x-ray fluorescence analysis.[15] The analysis of variance study on the raw shale concentration results show that for the oil yield 63% of the variation was on the daily level and 37% on the hourly level. This implies that a single sample cannot be representative of the oil yield over the 30-day period. However, since the amount of variance on the 1-hour and 8-hour levels is low, a composite sample need be taken only once a day to determine the organic characteristics of the feedstock and retorted shale for that day's operations. A scan of the results for the 17 elements analyzed shows that over 60% of the variance for all these elements lies on the 1-hour or analysis level. None of the elements show daily variances similar to the Fischer assays. Thus, on a production level none of the elements analyzed till now vary the same way as the organic content of the oil shale. However, the analysis of variance results show that a representative sample for the inorganic and trace elements can be determined. Thus, the grand mean for the retort month is a reasonable average for that month. Also, the relative standard deviations for the analysis of the elements is about 10%. This amount of analytical error is tolerable for most environmental studies. Yet, this amount of imprecision often contributed to the majority of the variance in the average. This means that for these elements, oil shale feedstock is quite uniform and homogeneous.

The same analyses have been made on the retorted shale and the same conclusions made for the raw shale apply to the retorted shale. In fact, the retorted shale is even more uniform than the feedstock. Fox and coworkers at the Lawrence Berkeley Laboratories have recently completed an analysis program of a core taken from the U.S. Naval Oil Shale Reserve No. 1.[26] It is from the same stratigraphic section as the shale mined at Anvil Points. The range in concentration of the elements in the formation is significantly greater than what is shown in Table 1. This implies that mining, hauling and crushing blends the feedstock. It also implies that the raw shale contained in an in situ retort may not be as uniform as the feedstock for a surface retort. The best method for sampling an in situ retort is still to be defined because the proper studies have yet to be made.

An important distinction occurs between taking just one sample daily or weekly and preparing a composite sample from the hourly cuts. In the case of one sample, the uncertainties exhibited on the 1- and 8-hour levels are compounded into a total variance which can be quite large. If samples are taken hourly and then combined into a composite, then the variances on the lower levels are eliminated and the uncertainty should be similar to what is seen on the daily level in Table 1. Consequently, it is quite important to take hourly cuts but then combine the cuts into a reasonable composite sample.

TABLE 1. CONCENTRATION PARAMETERS OF PARAHO OIL SHALE
The Sampling Period is from August 23, 1977 through September 20, 1977

	Conc.	Grand	Grand	Grand Rel.	Range	Avg. Analysis	% of Variance			
Substance	Unit	Mean	Std. Dev.	Std. Dev. %		Rel. Dev. %	24 hr Level	8 hr Level	1 hr Level	Analysis Level
Oil	gpt	27.0	3.2	11.9	22.0-39.0	2.0	63.0	0.0	37.0	--
Water	gpt	4.4	1.7	39.0	1.6-11.4	15.0	0.0	93.0	7.0	--
Gas & Loss	gpt	2.2	0.6	28.0	1.0-3.7	20.0	0.0	26.0	74.0	--
Ca	%	12.3	1.5	12.0	7.2-15.0	13.0	3.0	0.0	0.0	97.0
Mn	ppm	313.0	34.0	11.0	191.0-380.0	10.0	12.0	0.0	0.0	88.0
Fe	%	2.13	0.21	10.0	1.2-2.5	9.2	6.0	0.0	0.0	94.0
Ni	ppm	32.0	3.0	9.5	18.0-36.0	6.6	0.0	0.0	55.0	45.0
Cu	ppm	35.0	4.0	10.1	20.0-40.0	6.6	8.0	22.0	2.0	68.0
Zn	ppm	83.0	24.0	29.0	40.0-180.0	9.8	14.0	0.0	68.0	18.0
Ga	ppm	7.0	0.8	12.0	4.0-8.0	7.6	18.0	0.0	32.0	50.0
As	ppm	44.0	5.6	13.0	26.0-58.0	8.7	25.0	0.0	23.0	52.0
Se	ppm	1.5	0.26	17.0	1.0-2.3	15.0	7.0	0.0	0.0	93.0
Rb	ppm	80.0	6.0	7.4	45.0-85.0	1.7	24.0	0.0	73.0	3.0
Sr	ppm	770.0	66.0	8.6	410.0-830.0	2.2	32.0	0.0	62.0	6.0
Y	ppm	12.0	1.2	10.6	6.2-14.0	4.9	8.0	0.0	49.0	43.0
Zr	ppm	56.0	14.0	25.0	26.0-120.0	8.3	10.0	0.0	80.0	10.0
Nb	ppm	5.7	0.5	9.7	3.3-6.6	2.4	19.0	0.0	72.0	9.0
Mo	ppm	23.0	2.5	10.8	13.0-28.0	2.3	0.0	0.0	89.0	11.0
Ba	ppm	480.0	67.0	14.0	240.0-670.0	1.7	14.0	0.0	84.0	2.0
Pb	ppm	24.0	3.1	13.0	15.0-35.0	3.2	0.0	26.0	65.0	9.0

Sampling Procedures for Surface Retorts -

Organic constituents--A sampling system for raw and retorted shale similar in design to the one used at Paraho[4] [14] should be available on all surface retorts so that samples for quality control and environmental studies can be secured. If this is the case, the daily average sample delivered by that sampling system should be a composite of 24 one-hour samples. This daily composite sample should be suitable for organic studies made on raw and retorted shale. A daily sample is what is normally used for most quality control experiments and this sampling period should be reasonable for most environmental tests on the organic constituents.

In organic constituents--A weekly composite sample of raw and retorted shale should be sufficient for most studies that need to be performed on the inorganic constituents in these materials. This holds for quality control and for environmental studies. The best way to secure the sample is to split 100 grams from the composite daily sample. These splits can be combined and blended on a weekly basis.

Liquid Materials

Conclusions -

The following conclusions are again based on the experiences encountered during the Paraho sampling program. Consequently, they apply primarily to surface retorts.

1. Concerning the liquid products, sampling these streams can only be done every 8 hours. The reason is that the water has to be separated from the oil by settling and the amount that settles out is about 3% or less of the oil. So accumulating 1 gallon of water often requires the settling of 500 gallons, which is about 8 hours of retorting.

2. Also, at Anvil Points, sampling oil and water at this interval requires the manipulation of numerous valves. This makes the procedure prone to human error.

Discussion on the Conclusions -

There is great difference between how much is known about the solid materials and the liquids. This difference is partly due to the difficulty in sampling the liquid products on a surface retort. This difficulty is reflected in the conclusions. All those for the liquids are based on practical limitations whereas the sampling for the solids is built on a scientific basis.

The conclusions on the liquid handling system at Paraho are partly based on hours of confusion and frustration. There is no continuous sampling system for the liquids as there is for the solids. Even if such were available, the small amount of water produced makes it even more difficult to secure a sample of that material. During the Paraho study, securing a sample of the liquid product water from one shift was so difficult that in some instances it was not obvious that the proper tank was being sampled. Another situation also dictates against sampling the liquids more often than every shift. As is discussed in the HANDLING AND PRESERVATION section, the water and oil require much handling immediately after sampling. The water has to be separated from the oil, splits have to be prepared, and some splits bubbled with N_2. All this typically takes about two or three hours. So processing the liquids at more frequent intervals, becomes difficult unless sufficient personnel are available.

Sampling water from in situ retorts may not present the difficulties that it does on surface retorts. This is because the amount of water produced is about equal to the amount of oil produced. Consequently, one is not faced with the problem of separating a small amount of water from the oil.

Sampling Procedures for Surface Retorts -

The following procedures are based on practical considerations and not on a chemical study of the liquid samples. Consequently, it is better to consider the following as opinions and not firm recommendations.

Oils--A continuous sampling system should be built into the product oil handling system of a surface retort. Special attention should be given to the materials used for construction of the system. Stainless steel and glass may be reasonable for organic constituents but reactions and adsorption may occur between these materials and inorganic constituents. Handling of the sample may make collection on an hourly basis impractical, however the oil sampling system should be capable of delivering 8-hour and daily samples.

Product Waters--On a surface retort, the small amount of water associated with the product oil makes the sampling of the water on a continuous basis impractical. Furthermore, sampling of water on an 8-hour basis is also difficult. In this case, a compromise will probably have to be made between securing a definite sample by a convenient method and a questionable sample by a difficult method. A reasonable procedure would be to deliver oil to 1-day holding tanks that would have sampling taps built into them at the floor. A sampling system should be designed so that a sample of product water could be secured from the tap with little pumping or diversion of the liquids in the tank. Each daily holding tank should have its own sampling system.

HANDLING AND PRESERVATION

Solid Materials

Conclusions -

1. Concerning the crushing and grinding of oil shale, it is difficult to pulverize the rock to less than 100 mesh, and this step can add contamination to the sample.

2. The crushing of surface retorted shales poses no problems because the solids have lost much of their mechanical strength. Preparation of retorted shale samples does raise considerable dust so handling procedures should be designed so that dust fractions of the retorted shale are not lost.

3. Blending of raw and retorted shales is easily achieved during preparation. No unusual precautions have to be taken to insure a homogeneous sample. In fact, these samples are among the most homogeneous of geologic specimens.

4. Surface retorted shale is more homogeneous than raw shale. The retorting evidently homogenizes the rock.

5. Many of the conclusions stated for surface retorted shale may not hold for *in situ* retorted shale because the retorting conditions are not uniform in the latter case. Also, temperatures in an *in situ* retort may reach the fusion temperature of the rock. The retorted shale in this case will become like basaltic cinders and grinding may become quite difficult.

Discussion on the Conclusions -

Conclusion 1 on crushing requires the attention of research groups. When being pulverized, if too much time is spent in the grinder, oil shale can become heated and partially retorted. Disk puverizers will especially cause fusion and partial retorting. Currently, this project uses a SPEX shatter box for pulverizing. If the grinding chamber is to be used for over 5 minutes, it is first cooled in a freezer. Concerning contamination, the abundances of trace elements in oil shale are low enough that contamination is possible from grinding and sieving equipment. Table 2 compares the concentrations of elements in our standard oil shale (OS-1) with estimates of the concentrations that can occur in the worst cases of contamination from grinding in a shatter box.[16 17] No sieves should be used; instead, grinding tests should be made on spare amounts of raw shale. Alumina is not dense enough to crush small shale particles; tungsten carbide is expensive. Thus hardened steel seems a reasonable grinding surface. In the worst case, it could add 10% to the concentration of Ni and Mn, and 5% to Fe, Cu, and Mo.[1]

Fox and coworkers have recently reported the results of using a planetary ball mill with sintered corundum grinding surfaces for pulverizing oil shale.[26] They found that a sample could be ground to between 100 and 200

TABLE 2. CONCENTRATIONS OF ELEMENTS IN OIL SHALE OS-1 COMPARED WITH ESTIMATES OF CONTAMINATION FROM GRINDING AND SIEVING MATERIALS
All Concentrations are in ppm

Element	Rock	Contaminants			
	Oil Shale OS-1	Sieve	Grinding Materials		
		Stainless Steel	Tungsten Carbide	Alumina	Hardened Steel
Al	34000		60	5000	
Ti	1400			30	
V	130		6		2
Cr	40			20	
Mn	270	3			50
Fe	19000	20	300	60	500
Co	12		150	60	
Ni	30	3			20
Cu	50		5		10
Ga	10			80	
Mo	30				5

TABLE 3. RESULTS OF HOMOGENEITY TESTS FOR Rb AND Sr ON THE STANDARD SHALE AND A SPENT SHALE

	Raw Shale		Spent Shale	
Target Size	0.500 g	300.0 μg	0.500 g	300.0 μg
Number of Samples	8.0	6.0	8.0	6.0
Average for Sr (ppm)	584.0	584.0	771.0	735.0
Std. Dev. for Sr (%)	24.0	90.0	17.0	23.0
Rel. Std. Dev. for Sr (%)	4.1	15.0	2.2	3.1
Average for Rb (ppm)	60.1	63.3	80.7	93.4
Std. Dev. for Rb (ppm)	2.7	1.9	1.5	4.4
Rel. Std. Dev. for Rb (%)	4.5	3.0	1.9	4.8

mesh in 1 hour. The amount of contamination produced was negligible. The only contaminant was a slight amount of aluminum.

Conclusion 2 on the dust raised from retorted shale appears at first to be a nuisance. However, recent analyses on the retorted shale baghouse dust collected at the Paraho retort have shown that Ni, Cu, As, Mo, and Pb are definitely higher in Paraho retorted shale dust than in the bulk retorted shale.[6] If this is because certain phases are more prone to dusting, then segregation can occur by raising considerable dust while handling retorted shale.

Conclusions 3 and 4 concern the homogeneity of oil shale. It is remarkable how uniform it is when pulverized to -200 mesh. Table 3 contains the results of analyses for Rb and Sr in raw shale (OS-1) and retorted shale (SS-2) by x-ray fluorescence.[3] In both cases the samples were pulverized to -200 mesh. The remarkable feature in the numbers is that the method which uses only 300 μg of sample gives results which have uncertainties similar to those of the method which uses 0.500 g.[3] Most analytical chemists would refuse to accept a 300 μg split as a representative portion of the sample. In the case of oil shale it appears that it is representative. Note that in the relative standard deviations there is a hint that retorted shale gives more certain concentration values than raw shale. This indication of retorted shale being more homogeneous than raw shale was confirmed when the concentrations for Prarho raw and retorted shale show that the concentration ranges and relative standard deviations for most elements in retorted shale are lower than in raw shale.[6] Surface retorts homogenize the solid materials.

Conclusion 5 on the retorted shale from in situ operations is exemplified in the problems that Fox and coworkers had in processing spent shale from the simulated in situ retorts.[7] In their studies and in most in situ retorts the process is a batch operation rather than a continuous process so little mixing of solid materials occurs. Securing a representative sample of the retorted shale was a definite problem in their study. Also, they suggest that Pb, and possibly Zn and Cu, were added to the retorted shale during the pulverizing and sieving operations.

The question of how to store the solid samples should be considered. For inorganic analyses, polyethylene containers that have been washed with 8M HNO_3 would be reasonable.[12] However, plastic bottles may contribute some organic contaminants and furthermore they do breathe so that volatile materials can be lost or gained. If organics or mercury are to be analyzed, then perhaps glass containers would be more suitable. In addition, samples collected for the analysis of volatile constituents should not be subjected to wide temperature fluctuations so storage of the sealed samples in a regrigerator is recommended.

Handling Procedures for Solid Materials -

The whole sample should be crushed to -10 mesh using jaw crushers and roller crushers. At this point, a suitable sized sample of not less than

25 g should be split for further handling. This split is further pulverized in a hardened steel shatter box to a grain size suitable for analysis. Typically the pulverized sample has a -200 mesh grain size. No sieves should be used; this is especially important for the retorted shale. Instead, pulverizing tests should run and the shatter box should be operated for an appropriate amount of time. If the time spent in pulverizing the sample extends beyond 5 minutes, then consideration should be given to cooling the pulverizer in a freezer beforehand. Storage should be in glass or conventional polyetheylene bottles that have been rinsed in 8M HNO_3 at least overnight. If the analysis includes volatile constituents, storage should be in a refrigerator.

Liquid Materials

Conclusions -

1. Concerning the liquid products, there is a distillation of the oils and waters from solids in surface retorts so that minimal particulate matter occurs in the liquids. This makes filtration of the samples unnecessary. This is not the case for *in situ* retorts.

2. Handling of the oils and waters cannot be done in a uniform fashion for all studies. Some studies require the liquids to be bubbled with N_2, while others don't. Some require freezing, others refrigeration. Some require storage in glass, others in plastic.

3. The waters cannot be acidified since they contain appreciable thiosulfate and this decomposes at low pHs resulting in the formation of free sulfur.

4. Water samples can be held under refrigeration and freezing for over a year without decomposition. However, once opened the water does start changing within a month.

Discussion on the Conclusions -

The EPA Methods Manual on Water Analysis states that complete and unequivocal preservation of water samples is an impossibility.[18] Complete stability can never be obtained, and preservation techniques only retard the chemical and biological changes that continue after the sample is taken. To the EPA statement should be added that a universal water sample is an impossibility. A number of samples have to be taken and handling and preservation is dictated by the analytical objective. Both of these ideas are especially relevant to oil shale retort waters. In addition, there is a definite difference in the character of retort liquids from a surface retort and an *in situ* retort which is the basis for Conclusion 1. With regard to *in situ* retort waters, the program developed by Farrier and others on the Omega-9 retort water provides the primary basis for any analytical program on these waters.[19 20 21]

Conclusion 1 on the distillation is an important advantage in sampling surface retort liquids. Filtering the water using methods such as pressure filtration through Millipore filters can cause precipitation of some constituents.[27] Filtering oil typically requires vacuum or pressure methods and this may cause the loss of volatile constituents. When the Fischer assay oil was filtered, there was no residue in 600 ml of oil. The same was true of the water. These observations held true for the Paraho liquids. Concerning the separation of the two liquids, the oil predominates over the water by a ratio of 10 to 1 and the separation is clean. A good oil sample is easily procured. The water usually has oil in it. This can be stripped from the water by cooling the mixture to just above freezing and filtering through cotton or glass wool. The solid globs of oil are easily trapped.

For *in situ* retort liquids, separation of particulates is necessary. For water this is usually done by filtration through 0.45 μm Millipore filters.[7] [8] [19] In this case, the particulates have to be saved because they have been found to absorb trace metals.[7] [8] This should be done on warm oil so that the temperature does not fall below the pour point.

Conclusion 2 on handling and storage has to be addressed in any analysis program. In the Paraho project, four handling and preservation techniques were used: refrigerated, frozen, N_2 bubbled and regrigerated, and N_2 bubbled and frozen. At the time it was thought that that would be sufficient. However, some analysts felt that some splits should have been stored in glass for the analysis of organics and mercury in the liquids. Dr. Denney of the University of Colorado, who analyzes organic constituents in water, reports that specially cleaned glassware with special caps are absolutely essential for these analyses. The review of handling environmental samples also stresses this point.[12] For the analysis of Hg, some groups insist on glass,[9] while others find polyethylene acceptable.[8] The obvious conclusion is that the type of analysis dictates the handling and preservation methods to be used. Careful planning and recording of the actual procedures that are used are essential to the interpretation of the subsequent results.

Concerning Conclusion 3, this was observed by many people over the years; however, Dr. Leenheer's research group[23] was the first to confirm that $S_2O_3^=$ was a major constituent in the water and that it would disproportionate with elemental sulfur precipitating when the water was acidified. In the Paraho program, a number of product and process waters were collected and the $S_2O_3^=$ concentration ranged from 0.1 to 26 mg/ml as elemental sulfur.[6] A concentration of 26 mg/ml is a 0.41 molar solution of $S_2O_3^=$. In addition to $S_2O_3^=$, acidifying may cause carboxylic acids to precipitate. At first, the restriction of not acidifying is disconcerting because this is a standard method of assuring that trace metals are stabilized in solution.[24] However, the dissolved solids level in these waters is high, the pH is stabilized by NH_4HCO_3 in solution, and the oxidizing capacity appears to be stabilized by the various sulfur species. Consequently, little aging occurs as long as the sample is refrigerated.

The bases for Conclusion 4 are the results on the Paraho waters.[6] It appears that freezing preserves the pH and Eh values better than refrigeration. The deterioration of the waters after opening can be observed through the consistent rise in the specific conductance after one month of being opened. In this case, the first set of analyses were performed and the waters were returned to the refrigerator, then the analyses were performed and the waters were returned to the refrigerator, then the analyses were repeated about 30 days later.

Handling Procedures for Liquid Materials -

Special Procedures, Restrictions, and Comments -

1. The biases of the analyst come into play on the selection of containers. My preference is for conventional virgin polyethylene bottles (Nalgene type 2003). Other than FEP Teflon, these appear to be least contaminated with trace metals and least prone to transpiration of liquids and vapors through the walls.[12] [25] Oils and other organic material will attach polyethylene, but this attack is very slow if the samples are kept refrigerated or frozen.

2. The procedures described below are not suitable for the analysis of trace organics. In this case special procedures dictated by the analyst should be employed.[12] Also, all plastic materials should be considered at contaminants. Special consideration should be given to the type of cap used on the container.

3. In any program, more than one method of handling and preservation should be employed. The concentration values obtained by analysis apply only to that liquid at that time of analysis. Analysis of samples prepared by a number of methods helps to spotlight abberant results. This practice also may yield clues on how the sample has changed from the time of collection.

4. The procedures used below should be reasonable for the analysis of mercury. Fox and others[8] report that no loss of mercury was found for samples that were stored in airtight, acidwashed, polyethylene bottles at 4°C. However, in this case it is best to consult the analyst before collection of the sample.

Procedure for Oils--If the sample is taken from a continuous sampler, centrifuging is necessary to separate water and particulates. If the sample is taken from a holding tank, centrifugation may not be necessary. The sample is poured into at least 16 one-ounce polyethylene bottles that have been washed in 8M HNO_3, rinsed with deionized distilled water, dried, and tightly capped.[12] Equal numbers of the one-ounce bottles are prepared and stored in the following four manners: refrigerated, frozen, bubbled with N_2

and refrigerated, bubbled with N_2 and frozen. Upon analysis, the one-once bottles are used. Once opened, these samples will age, so the analyses should be performed within one month or a new one-ounce bottle should be used.

Procedure for Waters--If the sample is from an in situ retorting process, then it should be filtered through a 0.45 μm Millipore filter using a vacuum or N_2-gas pressure. The filter with the particulates should be saved for possible future analyses. If the micropore filtration is not needed, then cool the water and filter the sample through cotton or glass wool to remove insoluble organic material. The sample is poured into at least 16 one-ounce polyethylene bottles that have been washed in 8M HNO_3, rinsed with deionized distilled water, dried, and tightly capped.[12] Equal numbers of the one-ounce bottles are prepared and stored in the following four manners: refrigerated, frozen, bubbled with N_2 and refrigerated, bubbled with N_2 and frozen. None of the samples should be acidified. A portion of the unfiltered water should be poured into polyethylene bottles and refrigerated and frozen for future possible analyses. Upon analysis, the one-ounce bottles are used. Once opened, these samples will age, so the analyses should be performed within one month or a new one-ounce bottle should be used.

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FACTORS TO CONSIDER IN THE DESIGN OF A WATER QUALITY MONITORING NETWORK

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INTRODUCTION

The assumption that a water quality monitoring network can detect trends in water quality, check compliance with stream standards, and measure ambient water quality, etc., is incorporated into much of the enabling legislation for water quality management in the United States. This legal view of water quality monitoring envisions conclusive information being generated to actively guide government's water quality management efforts and, at the same time, report to the legislative bodies and the public the general water quality conditions and trends. When implemented, however, water quality monitoring is viewed more from a technical feasibility standpoint. That is, the problems involved in obtaining conclusive information with the available monies force many compromises and half measures--the consequences of which few fully understand.

Monitoring performed by an agency established by governmental action is, in many cases, conducted over a large geographic area (defined by political and not necessarily hydrologic boundaries) covering many miles of streams. Simply collecting samples in such a situation often becomes a major problem; so major, in fact, that it becomes an end in itself. In many cases, little thought is given to the representativeness of the water samples or types of data analysis techniques to be used or even the ultimate use of the data. Consequently, the majority of the resources are devoted to collecting data as it is the most immediate problem.

By using the majority of the monitoring resources to physically collect water samples, little monitoring resources are left to consider the representativeness of the sample in time and space, data analysis or data use. If a balanced (collection versus use) monitoring system were to be developed, the entire monitoring system must be examined and designed simultaneously, hence a systems approach.

The purpose of this paper is to review the monitoring system and then delineate the impacts that such a systems approach of monitoring will have on network design by considering the water quality variables to be monitored, the sampling location and sampling frequency.

MONITORING SYSTEM FRAMEWORK

The actual operation of a monitoring system can be categorized into five major functions:

1. Sample Collection
2. Laboratory Analysis
3. Data Handling
4. Data Analysis
5. Information Utilization

These five functions serve as the feedback loop from in-stream water quality conditions to water quality management decision making. A management agency is constantly making decisions (e.g., relative to site approvals, regulations, pollution abatement, etc.) that affect water quality. Without a monitoring feedback loop accurately documenting the effects of those decisions, the management's past success and future direction are uncertain.

Monitoring Network Design--is an overriding activity (covering the five operational functions listed above) that should carefully integrate sample collection (e.g., location and frequency) to the type of data analysis used to obtain the information required and actually utilized in decision making. Thus, the design of water quality monitoring networks must take into account the ultimate use of the data collected and the type and level of statistical analysis applied to the data.

FACTORS IN NETWORK DESIGN

Monitoring network design, as a planning/design type function which guides monitoring operations, can itself be broken down into three major components:

1. Selection of Water Quality Variables* to Monitor
2. Sampling Station Location
3. Sampling Frequency

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*The term water quality variable is used instead of water quality parameter because water quality is a random variable and can be defined by statistical parameters such as the mean and standard deviation. In addition, the term parameter is most often used to define constants of deterministic equations or models and can lead to confusion by identifying it as a random variable.

Each of these factors in network design affects all the monitoring system's operational functions listed previously and vice versa. The degree of impact, however, depends upon the purpose and goals of the monitoring system.

SELECTION OF WATER QUALITY VARIABLES TO MEASURE

The selection of the water quality variable to be sampled will depend to a large extent on the objectives of the sampling network and the background or frame of reference of the individuals responsible for developing the objectives of the monitoring network. When a sampling network has its primary objective to monitor compliance with stream standards, the variables sampled are the ones specified in the legislation, for example, dissolved oxygen (DO). DO is sampled because stream standards specify a minimum level which should not be violated. Dissolved oxygen and other variables deemed most important and included in stream standard legislation were those related to water supply, coliform bacteria, biochemical oxygen demand (BOD), temperature, turbidity, and suspended and dissolved solids, because most individuals entering the field of water quality management during the last few decades have a background in sanitary engineering.

Now that more individuals in professions besides sanitary (environmental) engineering are interested in water quality, the number of water quality variables which should be sampled routinely have increased. In fact, it appears that a month does not pass that yet another water quality variable must be sampled and included in a permanent sampling program. This variable-a-month syndrome cannot and should not be the major variable selection mode for a permanent, routine sampling program, but instead can be easily accommodated in the much discussed synoptic surveys.*

It can be said that both sampling location and sampling frequency can be developed independently of the water quality variable to be analyzed, as both location and frequency are specified for the collection of the water sample--the analyses are made later. However, both criteria are affected by the water quality variable being monitored. For example, sampling once a week at a single point in a river may be more than adequate for monitoring the relatively stable river temperature, but may be hardly adequate for monitoring rapidly varying coliform bacteria concentrations. Therefore, before a water quality monitoring network can be designed in a systematic fashion, the variables to be monitored should be specified so that their natural and/or man-made variation in time and space can be considered when designing the monitoring network. In addition to considering the water quality variables of interest, their respective units should be delineated as well. The network design varies tremendously if a daily mean (flow weighted) concentration is needed versus an instantaneous grab sample concentration, the former being a result of several samples with flow measurements equally spaced during a 24-hour period, while the latter being only a single sample (generally in the daytime between 8:00 a.m.-4:30 p.m.).

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*The increasing popularity of synoptic surveys with sampling agencies is probably due to the result that the surveys are in fact an application of a systems approach to water quality monitoring. Unlike the permanent, routine sampling programs, the objectives and the use of the data, the sampling locations, the sampling frequency, the variables to be sampled as well as the data analysis procedures are developed completely before the survey is undertaken.

In reality, the specification of the water quality variable to be monitored prior to initiating network design would be ideal. In practice, however, an already designed network is given and then one must know or determine what water quality variables can be accurately monitored with the existing network.

SAMPLING STATION LOCATION

The location of a permanent sampling station in a water quality monitoring network is probably the most critical aspect of the network design, but all too often never properly addressed. Expediency and cost compromises lead in many cases to sampling from bridges or near existing river gaging stations. Whether the single grab sample from the bridge or the gaging station is truly representative of the water mass being sampled is not known, but generally is assumed to be by both the collectors and users of the water quality data. Using river stage for estimating discharge, measurement anywhere in the lateral transect would indicate exactly the river discharge. However, this does not necessarily follow when measuring water quality variable concentrations. In fact, research indicates the opposite, that rarely will a single sample be indicative of the average water quality in a rivers' cross section.

Sampling locations for a permanent water quality network can be classified into two levels of design: macrolocation and microlocation, the former being a function of the specific objectives of the network and the latter being independent of the objectives but a function of the representativeness of the water sample to be collected.

The macrolocation within a river basin usually is determined by political boundaries (state lines), areas of major pollution loads, population centers, etc. Macrolocation can be specified, as well, according to percent areal coverage using basin centroids.[1] This methodology locates sampling points in a systematic fashion maximizing information of the entire basin with a few strategically located stations. Figure 1 is an example of locating sampling stations using basin centroids and sub-basin centroids with percent areal coverage as the criteria.

The procedure for locating sampling stations is derived by determining the centroid of a river system. Each contributing exterior tributary (this is a stream without defined tributaries) is given the magnitude of one; an interior stream resulting from the intersection of two exterior tributaries would have a magnitude equal to two. Continuing downstream in the same manner, as streams intersect, the resultant downstream stretch of river

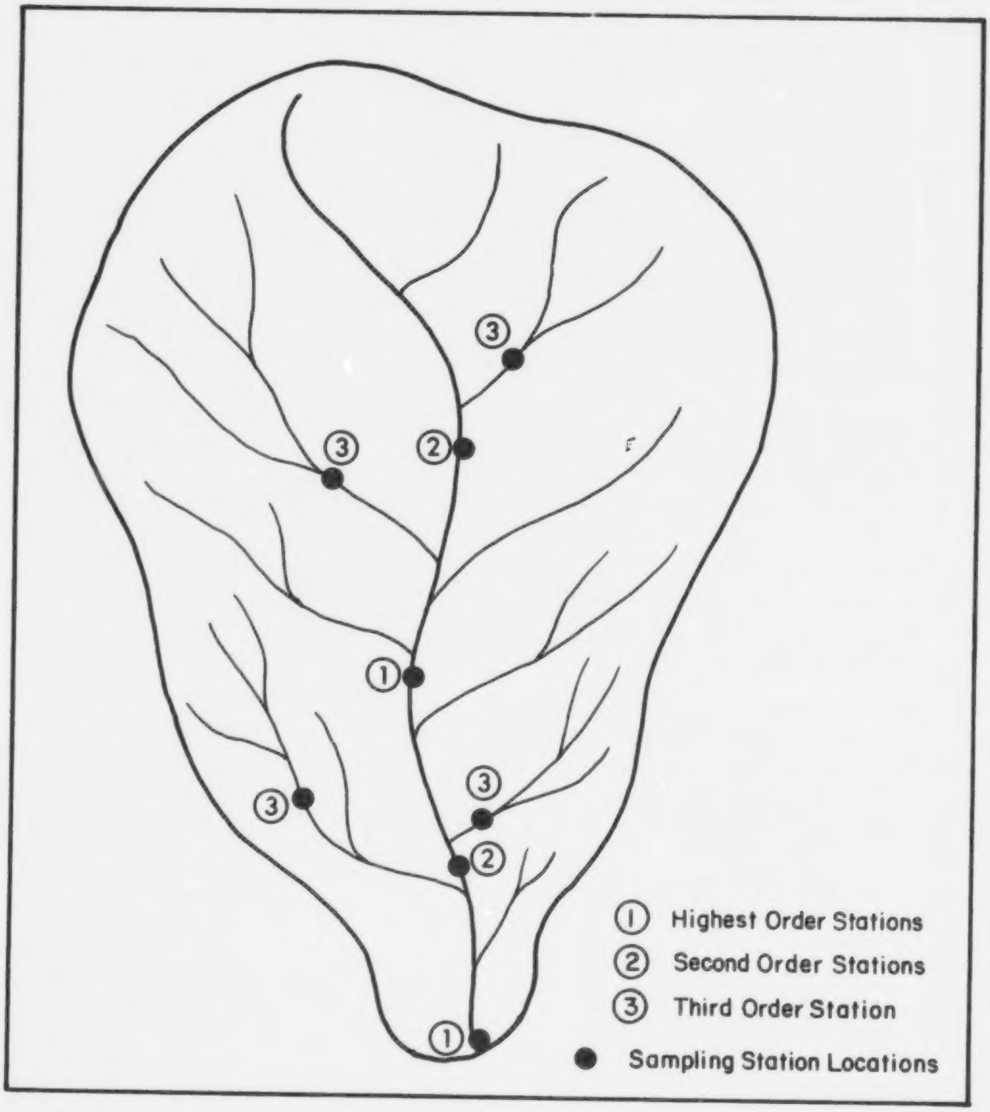

Figure 1. Macrolocation of Sampling Stations Within a River Basin Using the Percent Areal Coverage as the Criteria Specifying Location.

would have a magnitude equal to the sum of the magnitudes of the preceding intersecting streams. Finally, at the mouth of the river, the magnitude of the final river section will be equal to the number of contributing exterior tributaries--22 in Figure 1. Dividing the magnitude of the final stretch of the river by two, the centroid of the basin, 11 is calculated. The section of river having a magnitude equal to the centroid divides the basin into two sections and is the location of the sampling station with highest order (the assumption is made that there exists a sampling station at the mouth of the river basin). In many cases, when applying this procedure to a river basin, there usually is not a stream having a magnitude equal to the centroid. When this occurs, the stream segment having a magnitude closest to the centroid is chosen. The next order of sampling locations is determined by finding the centroids of the two equal sections above and below the initial river basin centroid. The procedure is continued finding the centroid of the sections of the river separated by preceding centroids until a percentage of areal coverage is attained.

The percentage of areal coverage specified by the monitoring agency is defined as the number of sampling stations divided by the magnitude of the basin. Intrinsic to this objective procedure is the concept of a sampling station hierarchy that orders the importance of each sampling station in the basin.[2] This provides a realistic methodology in which a rational implementation program can proceed: the most important stations (highest order) are built first and as the resources become available, additional stations can be built. As each succeeding hierarchy of stations are established the percentage of areal coverage is increased.

Having established the macrolocations within a river basin, the microlocation is then determined. The macrolocation specifies the river reach to be sampled while the microlocation specifies the point in the reach to sampled. This point is the location of a zone in the river reach where complete mixing exists and only one sample is required from the lateral transect in order to obtain a representative (in space) sample. Being a function of the distance downstream from the nearest outfall, the zone of complete mixing can be estimated using various methodologies.

Given the assumptions that a point source pollutant distribution in a stream approximates a Gaussian distribution, and that boundaries can be modeled using image theory, the following equation can predict the distance downstream in a straight, uniform channel from a point source pollutant to a zone of complete mixing.[3]

$$L_y = \frac{\sigma_y^2 u}{2 D_y} \qquad (1)$$

where L_y = mixing distance for complete lateral mixing,

σ_y = distance from point source to farthest lateral boundary,

u = mean stream velocity

D_y = lateral turbulent diffusion coefficient.

Unfortunately, there may exist in a given river reach no points of complete mixing* due in part to the random nature of the aforementioned mixing distance, inapplicability of the assumptions used in the determination of the mixing distance, or more often than not, not enough river length or turbulence to assure complete mixing within the specified river reach.

If there is not a completely mixed zone in the river reach to be sampled, there are three alternatives: (1) sample anyway at a single point and assume it is representative (this is the general procedure being applied today); (2) don't sample the river reach at all, because the data which would be obtained does not represent the existing river quality, but only the quality of the sample volume collected--in other words, the data is useless; (3) sample at several points in the lateral transect collecting a composite mean, which would be representative of the water quality in the river at that point in time and space.

If the sample is not representative of the water mass, the frequency of sampling as well as the mode of data analysis, interpretation and presentation and the realistic use of the data for objective decision making becomes inconsequential. In spite of this fact, criteria to establish station locations for representative sampling has received relatively little attention from both state and federal agencies responsible for water quality monitoring.

SAMPLING FREQUENCY

Once sampling stations have been located so that samples collected are representative in space, sampling frequency should be specified so that the samples are representative in time.

Sampling frequency at each permanent sampling station within a river basin is a very important parameter which must be considered in the design of a water quality monitoring network. A large portion of the costs of operating a monitoring network is directly related to the frequency of sampling. However, the reliability and utility of water quality data derived from a monitoring network is likewise related to the frequency of sampling. Addressing this anomaly Quimpo[4] summarized the significance of sampling frequency and stated that:

> On the one hand, by sampling too often, the information obtained is redundant and thus expensive, and on the other hand, sampling too infrequently bypasses some information necessitating an extended period of observation.

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*It should be noted that field verification of a completely mixed zone prior to locating a permanent sampling station can be easily done by collecting multiple samples in the cross section and analyzing the data using a well-known one- or two-way analysis of variance techniques.

Significant as sampling frequency is to detecting stream standards violation, maintaining effluent standards, and estimating temporal changes in ambient water quality, very little quantitative criteria which designates appropriate sampling frequencies have been applied to the design of water quality monitoring networks. In many cases, professional judgment and cost constraints provide the basis for sampling frequencies. All too often, frequencies are the same at each station and based upon routing capabilities, once-a-month, once-a-week, etc. and although possibly the only practical means to implement a sampling program considering the statistical background of data collectors, there do exist many quantitative, statistically meaningful procedures to specify sampling frequencies at each station.[5,6] The methods include specifying frequencies as functions of the cyclic variations of the water quality variable (Nyquist frequency), the drainage basin area and the ratio of maximum to minimum flow,[7] the confidence interval of the annual mean,[8,9] the number of data per year for hypotheses,[10] and the power of a test measuring water quality intervention.[11]

All of the aforementioned procedures can be applied to the design of a water quality monitoring network with each requiring a different level of statistical sophistication insofar as data requirements as well as assumptions applying.

One of the simplest approaches is to assume that the water quality variable concentrations are random, independent and identically distributed (iid) and determine the number of samples per year as a function of an allowable (specified) confidence interval of the mean annual concentration (this is analogous to the procedure for determining how many analyses of a water sample should be made to determine a reasonable estimate of the mean water quality variable concentration).[5]

$$n = \left[\frac{t_{\alpha/2}\, S}{R}\right]^2$$

where n = Number of equally spaced samples collected per year
$t_{\alpha/2}$ = Constant which is a function of the level of significance and the number of samples
S = Standard deviation of the water quality concentrations
R = Specified half-width of the confidence interval of the annual mean.

Using the same assumption, that the water quality variable is iid, the number of samples per year can be specified as a function of the data analysis procedure as well.[10] For example, if annual means were to be tested for significant changes using the difference in means, then to detect an assumed level of change, the number of samples can be specified.

A much more sophisticated procedure, representing a higher level of statistical analysis, is to recognize that water quality variables may not be iid, but highly dependent, not identically distributed, having seasonal variation, and determine sampling frequency as a function of the variability of the water quality variable time series after trend and periodic components have been removed. Unfortunately, other than mean daily discharge, data bases of water quality variable of sufficient number, reliability and length are generally not available for application of this procedure.

Once a uniform sampling frequency criterion is selected it can be utilized to objectively distribute sampling frequencies within a water quality monitoring network. For example, the expected half-width of the confidence interval of the annual mean (for specifying sampling frequencies) approach can be applied basin-wide in a consistent fashion by specifying equality of these expected half-widths at each sampling station. Thus, stations where water quality varies tremendously will be sampled more frequently, than stations where the water quality varies little. With reference to Figure 2 which is a plot of the expected half-width of the confidence interval of mean log river flow versus the number of samples per year, the number of samples collected at each station within the river basin for a given R are determined by drawing a horizontal line through R and reading the number of samples on the abscissa axis below the intersections on the horizontal line with each curve. Figure 2 may also be used in an iterative fashion to specify sampling frequencies at each station when a total number of samples from the basin is specified. For example, if only N samples per year would be collected and analyzed, a value of R is assumed and a line is drawn horizontally; the number of samples specified by the intersection of the curves are summed and compared to N. If the sum were not equal to N then another estimate of R would be made until the sum of all the samples is equal to N.

It should be noted that the expected half-width of the annual mean is not the only statistic that can be used to specify sampling frequencies; the expected half-width divided by the mean is a measure of relative error and may be more appropriate when assigning sampling frequencies in a basin where water quality varies tremendously from river to river.

When developing sampling frequencies, one must keep in mind two very important cycles which can have immense impact on water quality concentrations--the diurnal cycle and the weekly cycle. The effect of the diurnal cycle (which is a function of the rotation of the earth) can be eliminated by sampling in equal time intervals for a 24-hour period and the effect of the weekly cycle (which is a function of mans' activity) can be eliminated by specifying that sampling intervals for a network cannot be multiples of seven--occasional sampling on weekends would be necessary.

Perhaps, the major impact between network design in terms of variables to be monitored, sampling location, and sampling frequency and the operational monitoring functions is in the area of data analysis and, consequently, ultimate value of the monitoring network information. Any sampling program that is to generate conclusive results from observing a stochastic time series (water quality concentrations) must be well planned and statistically designed. Statistically designed implies that the sampling is planned (in proper locations and numbers) so that the statistical analysis

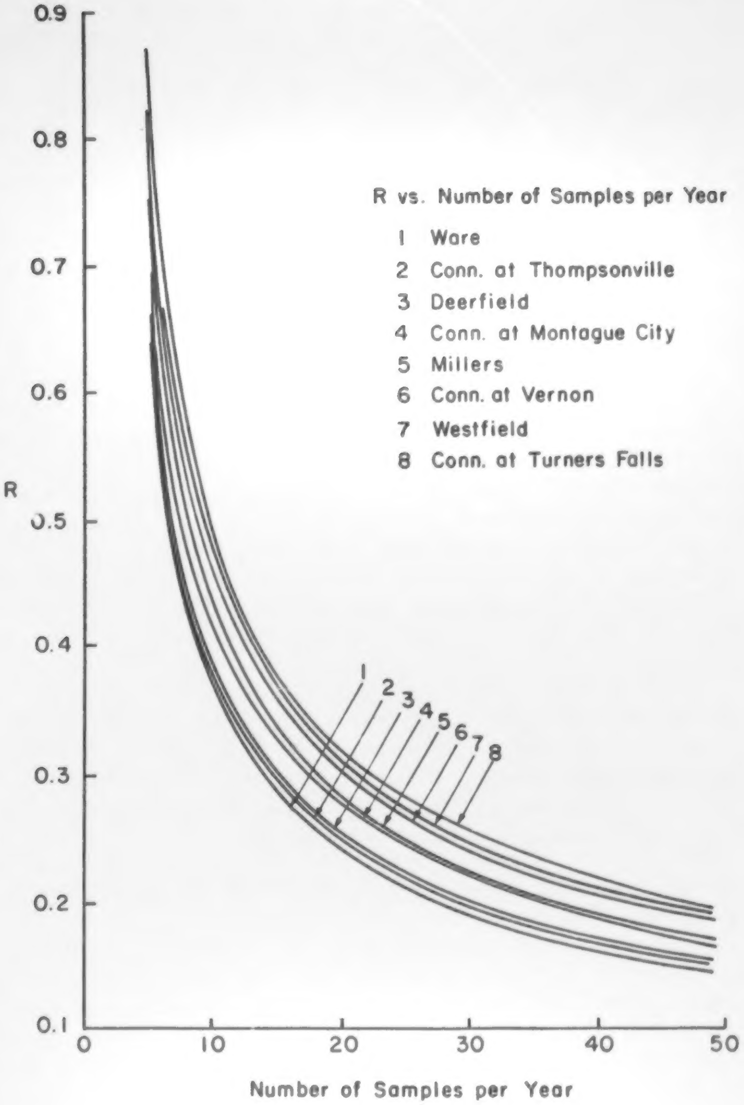

Figure 2. A plot number of samples per year of the expected half-width of the confidence interval of mean log flow, R, versus number of Samples for Several Rivers in the Connecticut River Basin.

techniques chosen will be able to yield quantitative information. Thus, the data analysis techniques (level and type of statistics) to be used must be defined in order to know how to compute proper sampling frequencies, locations, etc.

SUMMARY AND CONCLUSIONS

The previous discussion has pointed out many problems associated with not designing a monitoring system in a systems context. Perhaps the major concern is that all aspects of a monitoring program should match in terms of accuracy. For example, it would not be wise to use time series analysis on nonrepresentative, grab sample data--the system would be providing excessive accuracy in one segment compared to the accuracy in another segment.

In a similar manner, it may be unrealistic to encourage use of more sophisticated sample collection and laboratory analysis techniques if the data is not to receive a thorough statistical analysis.

We cannot continue to test hypotheses, make decisions, justify additional billions of dollars to be spent on pollution control, etc. using water quality data which are collected, only in the daytime, not flow weighted, several times a year, from locations which are not completely mixed and using lab analyses procedures which may have more variation in their results when analyzing the same sample than the ambient variation of the water quality variable in the river.

Perhaps an even larger concern to those in monitoring network design is the use of water quality standards that generally ignore statistics. This lowers the value of any information, from a compliance viewpoint, to that of spot checks. Incorporating water quality means and variation into standards would greatly facilitate incorporating more statistics into monitoring. This would have the effect of tying network design to data use in a much more concrete, statistical manner than is now possible. It would also encourage use of the system approach to network design as there would be a statistical thread moving through the entire monitoring operation.

ACKNOWLEDGMENTS

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QUANTITATION OF INDIVIDUAL ORGANIC COMPOUNDS IN SHALE OIL

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ABSTRACT

A serious and largely unknown complication of developing alternate fuels such as shale oil is the potentially deleterious impact on the environment. Identification and quantitation of toxic organic compounds in the feedstock, process streams, and plant effluents will become increasingly important as mutagenicity testing on chromatographic fractions generated from various fuels and effluents expands. In preparation for certifying a Standard Reference Material for toxic constituents in alternate fuels, our laboratory has been investigating various techniques for quantitating individual organic compounds in shale oil. Emphasis has focused on acid-base extraction and high performance liquid chromatography as independent methods of shale oil fractionation. Gas chromatographic, gas chromatographic mass spectrometric, and high performance liquid chromatographic methods have been used to quantitate several phenols, *N*-heterocyclics, and polynuclear aromatic hydrocarbons in shale oil.

INTRODUCTION

In order to enhance the accuracy of environmental measurements associated with the development of alternate fuels such as shale oil, the Organic Analytical Research Division of the National Bureau of Standards is developing the analytical expertise necessary to certify the concentrations of several phenols, N-heterocyclics, and polynuclear aromatic hydrocarbons in shale oil and to issue it as a Standard Reference Material (SRM) for shale oil. The accurate quantitative analysis of individual toxic organic compounds in alternate fuels will become increasingly important as mutagenicity testing on chromatographic fractions generated from these fuels and effluents expands. Without accurate measurement, scientists cannot correctly relate health effects to levels of pollution, engineers cannot correctly assess the effectiveness of various control technologies, and the government cannot correctly make policy decisions which require compromises among conflicting demands of environmental protection, energy conservation, and public as well as economic health.

Numerous studies on the qualitative analysis of shale oil and coal liquids appear in the recent literature. Unden et al.[1] characterized the acidic and basic fractions of shale oil by GC-FTIR. Dark et al.[2] used HPLC and LC-MS for the characterization of coal liquefaction products. Clark et al.[3] used both solvent extraction and chromatographic techniques for the isolation of alkanes and polynuclear aromatic hydrocarbons from shale oil. Jackson et al.[4] characterized hydrocarbon types in shale oil distillates with the use of a hydroboration-acid absorption technique. The major emphasis of these studies has been qualitative, however, rather than accurate quantitative analysis of individual compounds.

In prepartion for certifying a Standard Reference Material for toxic constituents in alternate fuels, we have been investigating various techniques focused on acid-base solvent extraction and high performance liquid chromatography as independent methods of shale oil fractionation as a prelude to quantitative determinations of individual compounds by various gas chromatographic, gas chromatographic-mass spectrometric, and high performance liquid chromatographic methods. A comparison of results obtained by these various methods will be the subject of this paper.

EXPERIMENTAL

Shale Oil Sample

The shale oil analyzed in this work is from a 150-ton retort for *in situ* simulated combustion operated by the Laramie Energy Research Center, Laramie, Wyoming. The shale is from the Mahogany zone of the Colorado Green River formation. An 8 L sample of this shale oil was obtained by NBS from oak Ridge National Laboratory, Oak Ridge, Tennessee. The shale oil underwent centrifugation at Oak Ridge to separate water (∿40%) and sludge from the oil. A subsample of 1 l was removed from the 8 l bulk sample. Aliquots of ∿5 ml each were sealed in amber glass ampoules for subsequent analyses. The samples were analyzed to measure the concentration (μg/g) of pyrene, fluoranthene, benzo(a)pyrene, phenol, *o*-cresol, 2, 4, 6-trimethylpyridine, and acridine.

Extraction

Acid-base Extraction--The shale oil sample was separated into three fractions (acids, bases, and neutrals) using an extraction procedure adapted from Schmeltz.[5] For the determination of the PAHs, an additional liquid-liquid partition step using dimethylformamide (DMF)/water and hexane was utilized to remove the aliphatic hydrocarbons from the PAH neutrals. This procedure for the isolation of PAHs in complex mixtures has been previously reported by Bjørseth.[6]

HPLC Extraction--The shale oil sample was diluted (∿0.1 g/ml) prior to fractionation on a preparative scale aminosilane column (30 cm x 7 mm i.d.). A sample containing from 10-15 mg of shale oil was injected onto the column using a loop injector. A mobile phase flow rate of ∿5 ml/min was employed. Standards of the compounds to be determined and the compounds utilized as internal standards were injected to determine the appropriate elution volumes for fraction collection. After collection of the fractions in 15-

or 40-ml centrifuge tubes, the fractions were reduced to 50-500 μl by passing N_2 over the sample.

Quantitative Analysis--Chromatographic conditions for the LC, GC, and GC/MS quantitation of individual compounds are summarized in Table 1. Details of these analyses are reported elsewhere.[7]

TABLE 1. CHROMATOGRAPHIC CONDITIONS FOR QUANTITATION OF INDIVIDUAL SHALE OIL CONSTITUENTS

Compound Class	Gas Chromatography	Liquid Chromatography	Gas Chromatography Mass Spectrometry
Polynuclear aromatic hydrocarbons	30 m WCOT Carbowax 20 M	Octadecylsilane 70/30 CH_3CN/H_2O and 40-100% linear gradient	30 m SCOT SE-30 and 30 m WCOT SE-52
Phenols	30 m WCOT SP-1000 and Carbowax 20 M capillary	Octadecylsilane 40/60 CH_3CN/H_2O	6 ft. 0.1% SP-1000 packed column
N-heterocyclic compounds	30 m WCOT SP-1000	Octadecylsilane 0-50% linear gradient CH_3CN/H_2O	30 m WCOT SP-2100 and 17 m WCOT SE-52

RESULTS AND DISCUSSION

Quantitative determinations of individual components in a complex matrix such as shale oil require that the sample be cleaned up prior to analysis to remove nonanalyte interferences. This sample cleanup step has traditionally involved a solvent extraction step such as that reported by Schmeltz.[5] This extraction step is a laborious procedure which requires 1-2 man days to generate the acidic, basic, and neutral oil fractions. When a standard addition technique involving three or four standard additions is used for quantitation, the time spent on sample preparation becomes prohibitive. Furthermore, once the extraction step has been completed, the sample must be subjected to a high resolution chromatographic separation to allow individual components to be quantified free from interferences.

The shale oil sample described above was analyzed for the following compounds within each class (the specific compounds were arbitrarily selected as being representative of the class of compounds and many are EPA priority pollutants): Acids-phenol and o-cresol, bases--2, 4, 6-trimethylpyridine and acridine, and PAHs--fluoranthene, pyrene, and benzo(a)pyrene. Quantitative determinations for the compounds in the acid/base solvent extracted fractions were performed by gas chromatography or, where additional specificity was required, by gas chromatography/mass spectrometry with selected ion monitoring. The results of these determinations are presented in Table 2, under the heading "Acid/Base Extraction."

A novel, rapid method of preparing shale oil fractions for subsequent quantitative determinations has been developed which involves a high performance liquid chromatographic separation of the shale oil on a preparative scale aminosilane (µbondapak NH_2) column. The compound(s) to be determined can easily be eluted selectively by modifying the composition of the mobile phase. By judiciously adjusting the mobile phase composition from 100 percent hexane to 100 percent CH_2Cl_2 it is possible to elute a wide range of compounds from nonpolar PAHs to the more polar phenols and N-heterocyclics. An example of the HPLC fractionation of shale oil to generate a PAH fraction is ullustrated in Figure 1. Standards of the compound(s0 to be determined are run prior to fractionating the shale oil to determine the appropriate elution volume for fraction collection. This standard run is seen as the lower chromatogram in the figure. Depending on the particular compound being determined and its elution volume, the fraction can generally be prepared in less than an hour. The shale oil fractions thus obtained were analyzed for the individual compounds of interest by various high performance liquid chromatographic, gas chromatographic, and gas chromatographic/mass spectrometric techniques (see Table 1). The results of these determinations are shown in Table 2. As can be seen, the agreement among values obtained by independent quantitative techniques is excellent at the 95 percent confidence level. A comparison of results from determinations on fractions obtained by an acid/base extraction vs. those obtained from the HPLC generated fractions are also in excellent agreement. Although the "true" or "actual" concentrations cannot be verified with current state-of-the-art methodology, the intralaboratory precision obtained using independent techniques of shale oil fractionation and quantitation give us confidence in the results obtained.

For many environmental analyses, there is little or no knowledge of comparability of data from different laboratories and, in most cases, probably little knowledge of intralaboratory precision. In order that the data from different laboratories and methods be useful and reliable, there must be a basis for intercomparability. Furthermore, unless the quantitative data can be related from one laboratory to the next, environmental standards can be neither set nor enforced. Research leading to the development of Standard Reference Materials and the correct use of these SRMs are one means for ensuring the comparability of these measurements.

Aliquots of the shale oil sample were sent to several laboratories currently involved in characterizing alternate fuels. The laboratires were requested to determine the concentrations of the phenols, N-heterocyclics, and PAHs mentioned above. Preliminary results of this limited interlaboratory exercise are presented in Table 3. The scatter of the results indicate the variability of state-of-the-art quantitative analyses for individual

TABLE 2. SHALE OIL ANALYSIS
(ppm, 95% confidence level)

		HPLC Extraction Quantitation by			Acid/Base Extraction Quantitation by
Compound	LC	GC	GC/MS	GC	GC/MS
Pyrene	108.0 ± 16.0	101.0 ± 4.0	102.0 ± 9.0	94.0 ± 10.0	--
fluoranthene	53.0 ± 6.0	55.0 ± 6.0	62.0 ± 5.0	75.0 ± 5.0	--
Benzo(a)pyrene	21.0 ± 2.8	--	21.0 ± 5.0[a]	--	24.0 ± 2.0
Benzo(e)pyrene	--	--	20.0 ± 6.0[a]	--	22.0 ± 5.0
Phenol	383.0 ± 50.0	387.0 ± 26.0	416.0 ± 28.0	--	334.0 ± 63.0
O-cresol	330.0 ± 34.0	334.0 ± 86.0	350.0 ± 16.0	--	322.0 ± 45.0
2, 4, 6-trimethyl pyridine	--	912.0 ± 26.0	1214.0 ± 64.0	988.0 ± 56.0	--
Acridine	6.0 ± 2.4	--	4.4 ± 0.3	--	--

[a] Internal standard of perylene used instead of standard addition.

HPLC Fractionation of Shale Oil

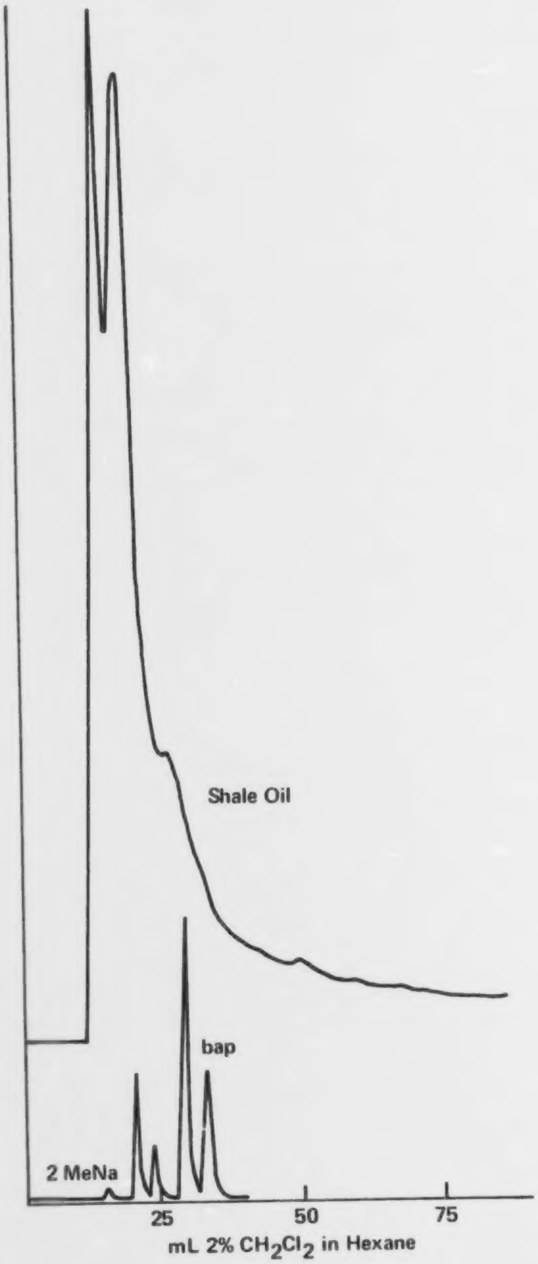

Figure 1. HPLC Fractionation of Shale Oil--PAHs

TABLE 3. INTERLABORATORY COMPARISON OF RESULTS OF SHALE OIL ANALYSIS

Compound	NBS[a]	2	3	4	5	6	7
Pyrene	107	155	360	150	168	212	141
Fluoranthene	61	102	220	80	108	104	112
Phenol	395	392	180	--	--	--	399
O-cresol	338	350	150	--	--	--	381
2, 4, 6-trimethylpyridine	1060	468	460	--	950	--	1092

[a] Results reported by NBS represent the mean of values obtained by GC, GC/MS, and HPLC.

compounds in a complex matrix. It also stresses the need for a SRM, such as the shale oil, which laboratories responsible for quantitative measurements can use to gauge the accuracy of their analytical methods.

CONCLUSIONS

Quantitative determinations for individual organic constituents in a shale oil have been accomplished using two independent fractionation techniques and various quantitative methods. A novel HPLC technique for the rapid separation of shale oil into fractions for the analysis of phenols, N-heterocyclics, and polynuclear aromatic hydrocarbons has been presented. Intralaboratory precision for the determination of single species concentrations in a shale oil was excellent, and is expected to result in the release of a shale oil SRM in the near future, to be certified for several compounds in each class. The results of a preliminary interlaboratory exercise on the quantitative determinations of individual compounds in shale oil emphasize the need for such a standard.

In order to specify procedures adequately, it has been necessary to identify some commercial materials in this report. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material identified is necessarily the best available for the purpose.

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ISOLATION AND IDENTIFICATION OF ORGANIC RESIDUES FROM PROCESSED OIL SHALE

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ABSTRACT

The purpose of this study was to identify characteristics of organic residue from processed oil shale. Processed oil shale samples from the Union B, Paraho and TOSCO II processes have been extracted by using organic solvents in a soxhlet apparatus and by mixing shale samples with water. Sample extraction residues were identified by gas chromatography coupled with mass spectrometry (GC/MS).

INTRODUCTION

Western shale organic content estimates have been reported by USGS and BLM since the turn of the century. More recently, because of increasing attention to this fossil fuel reserve, methods and estimates of oil extractability and characterizations of organic constituents have been reported. In the past decade many investigations of oil shale kerogens and bitumens have focused on macroconstituent determinations. Others report development of laboratory regimes designed to isolate and identify the organic residue from processed oil shale. More intensive investigations of the organic matrix of products and wastes derived from shales, tar sand, coal, and high boiling crude oil distillates are also reported. Isolation methods have included liquid/liquid (L/L) extractions, thin layer chromatography (TLC), and liquid column chromatography (LC). Extraction and elution solvents employed have ranged from low polarity solvents (i.e., benzene, cyclohexane, hexane(s), pentane) through polar solvents (i.e., acetone, ethanol, methanol, CH_2Cl_2, $CHCl_3$). Basic, neutral and acidic isolation conditions and TLC/LC media have been used. Reported identification methods employed include NMR, MS, IR, HPLC, GC, and GC/MS. A selection of these investigations are summarized in tables appended to this paper (Tables A1-A5 including associated references).

METHODS AND PROCEDURES

Approach

Two approaches for extracting organics from spent shales were employed. First, organic solvents following classical organic chemistry procedures were used to extract and concentrate the organic materials remaining in the processed shales. Second, water was used for extraction. The water extracted organics were either sorbed by a resin and eluted with polar solvents or partitioned to organic solvents by liquid/liquid extraction prior to concentration and GC/MS identification of constituents.

A low level of light was maintained during these laboratory procedures. All laboratory equipment utilized was made of glass, metal or Teflon. Reusable glassware was washed in four organic solvents of decreasing polarity, acid/base washed, distilled water rinsed and oven dried. Extraction and concentration glassware was heated for one hour at 550°C.

Organic Extraction

As cited in the literature, soxhlet extraction solvents have included redistilled (in glass) pentane, cyclohexane, benzene, and benzene:methanol mixtures. The more polar concentrated methanol extracts have been used directly in the Ames test for mutagenicity. (Presentation of this research is included in the symposium paper entitled "Detection of Chemical Mutagens in Spent Oil Shale Using the Ames Test [Dickson et al.].)

The soxhlet extraction method was employed to develop extracts for GC/GC-MS investigations. 400 grams of processed oil shale samples were charged to each soxhlet and 1.2 ℓ leaching solvent was used. Sample characterization, leaching solvent, and extraction conditions utilized are summarized in Table 1.

Each soxhlet extraction sample was divided in half. One part was then concentrated by flash evaporation (Buchler Instruments) and the other part concentrated by Kuderna Danish heat evaporation (500 ml Kontes with a 10 ml concentration tube and macro Snyder condenser). The concentrated solutions (~10 ml) were then further concentrated to 4 ml at room temperature using a gentle stream of nitrogen.

Thin layer chromatography (TLC) was utilized to fractionate some of the concentrated soxhlet extracts. Concentrated extracts equivalent to a soxhlet charge of 1.0 kg were applied to silica gel plates (EM Laboratories Inc., 20 cm x 20 cm x 2 mm, PLC 60F-254 Plates); and developed in benzene: cyclohexane (3:2). Separated compounds were visualized by means of an ultraviolet hand lamp. As observed in ultraviolet light (~254 hv), the ten compounds included in a standard PAH mixture resolved into five fractions. Based on the TLC resolution of the PAH standard mixture, the resolved sample TLC plates were fractionated as <0.1, 0.1-0.25, 0.25-0.6, 0.6-0.8 and >0.8 of the developed solvent front (TLC R_f values). The silica gel as fractionated was scraped from the TLC plates and the associated resolved sample components were eluted in methanol. To ensure a maximum recovery of the sample components from the scraped silica gel fractions [illegible] [illegible] VWR Scientific) [illegible] The silica gel was removed from [illegible] by [illegible] pheres (GFC filters). The filtered sample fractions were concentrated to a

TABLE 1. CHARACTERIZATION OF EXAMPLE SAMPLES AND SOXHLET EXTRACTION OPERATING CONDITIONS

	Sample Extracted				Soxhlet Operation		
[illegible] & [illegible][a]	Sieve Fraction	% H_2O[b]	% Volatiles[c]	Benzene Leachables (ppm)[d]	Leach Solvent	Time (Days) @ 3 min/ cycle	GC/GC Trace/Spectrum Figure(s) and/or Comments
[illegible]	<1/4"	0.5	≅14	49,600	Pentane	3	TAR Problem
TOSCO [illegible]	<1 mm	1.9	≅ 9	1,900	Methanol after Benzene	3	Mutagenicity of this extract reported by Dickson et al., this symposium
TOSCO DcAR[e]	<1 mm	1.9	≅ 9	1,900	Benzene	3	Figure 1 Chromatography
Paraho[e] Dkd 60-80	<1 mm	1.5	≅ 7	150	Benzene TLC Methanol	≅4	Figure 2 Chromatograph of TLC fraction 0.6-0.8 R_f
Union D11	<1 mm crushed	1.3	≅15	77,300	Benzene and Benzene :Methanol	≅3 ≅3	These extracts could not be concentrated to less 10 mℓ due to TAR matrix

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[a] The shale samples are identified by process source but are representative only of early surface retorting investigations and should not be considered reflective of commercial scale processed shales.

[d] Determined by further drying of ground air dried samples at 103°C until approximately constant weight (total samples = 30, maximum CV = 4%).

[c] Determined by heating dried samples (from b above) at 550°C until approximately constant weight (total samples = 35, maximum CV = 7%). Includes ammonia, CO_2, etc. as well as organics.

[d] ppm: parts dried benzene leachables per million parts leached shale (by weight). Data is comparable to Schmidt-Collerus (1974) procedure.

[e] Paired samples from different intermediate sources.

nitrogen atmosphere. The separated TLC silica gel showed no fluorescence under the UV hand lamp.

Water Extractions

A 55 gallon Teflon lined drum was used as a mixing chamber for the water extractions. Mixing run compositions varied from 5 to 50 kilograms dry spent shale (<1 mm sieve) and from 10 to 100 liters of water. After mixing (from 2 to 12 hours) and investigation of post mixing physical settling characteristics (~90 min), 20 liters of near surface water was drawn off and filtered (Whatman Qualitative #2).

Extracted organics in these filtered water samples were sorbed with nonionic sorption resin (XAD-2). A CH_2Cl_2 liquid/liquid extraction routine was used as a comparison extraction method (EPA, 1977). Preliminary investigations using distilled water and known concentrations of PAH indicate that XAD sorption and L/L extraction transfer efficiencies were comparable. Webb (1975) reported that the differences between XAD-2 and $CHCl_3$ extraction efficiencies were less than 10 percent for the low molecular weight PAH compounds that he studied.

For preparation of the XAD-2 resin, 3 soxhlet extractions of 8 hours each were required. The XAD-2 resin was placed in a soxhlet and extracted first with acetonitrile, then ether, and finally with methanol. The resin was stored under methanol as required.

A glass chromatography column (10 x 1 cm id) with a 20 liter delivery tank was used for the XAD-2 resin. Silanized glass wool plugs were used on each side of the XAD-2 column resin pack. After activation of the resin with 40 ml deionized water ("Milli Q System"), 20 liter sample water extracts were passed through the column at 30 ml/min. Stepan and Smith (1977) report that higher PAH sorption efficiencies are possible with lower column flow rates than used here. The column resin was eluted with 30 ml of ether. $MgSO_4$ was used to remove water from the ether elutants. The water free ether elutions were then concentrated to 0.1 ml in a gentle stream of nitrogen. A detailed description of XAD preparation and column operations is presented in Junk et al. (1974).

GC/MS and GC Identification

Organics in the extracted and concentrated samples were identified with a Hewlett-Packard gas chromatograph-mass spectrometer (HP 5985 GC/MS System). A 10 meter glass capillary column coated with SP2100 was temperature programmed from 90°C to 250°C at 5°/min to resolve sample components. The mass spectrometer ionization voltage was maintained at 70 ev. Injection port and transfer line temperatures were 250° and 275° respectively.

A HP-5750 gas chromatograph fitted with a 180 cm x 0.3 cm stainless steel column packed with 10 percent SP2100 on 80/100 mesh Supelcoport was used for sample screening work. This column performed adequately yet at higher operating temperatures (>250°) column bleed was excessive. A liquid crystal packed column was also used to resolve a standard PAH mixture for comparison with the above study columns. The liquid crystal column yielded excellent resolution, even of the larger molecular weight isomers. GC/MS library identifications were possible with injections equivalent to less than 1 ng for each PAH in the standard mixture. However, according to the literature review, liquid crystal columns have not been used to resolve complex environmental samples (see appendix).

RESULTS AND DISCUSSION

The higher organic content shale samples investigated in this study produced a tarry matrix during extractions with benzene, cyclohexane, pentane or with benzene:methanol mixtures. The celulose soxhlet thimbles can have "tar" plugging problems. Concentration of these tarry extracts often led to the development of an asphaltic-like tar complex. Similar tar extraction and concentration problems have been reported by researchers working with raw oil shales, bitumens, kerogens and related substitute crude oils. Various laboratory methods have been devised to investigate tar matrices (see appendix tables). Consequently, the isolation and identification of organic residue from processed oil shale reported in this paper does not include samples with tar matrices capable of limiting concentration of extracts to <4 ml. The samples are also reflective of the lower organic content processed shales.

Kuderna-Danish heat evaporation and vacuum evaporation allow quantifiable organic separations. Comparison of GC traces of split extracts concentrated by these methods show slight differences in relative peak responses. Junk and coworkers (1974) have noted differential concentration efficiencies of low molecular weight PAH when comparing differing Kuderna-Danish designs.

GC/MS of Soxhlet Extracts

A sample of benzene soxhlet extract has been resolved into more than 120 peaks as shown in Figure 1. The GC trace was obtained from the equivalent to the benzene leachables from about 50 mg of a shale sample (see Table 1 for description of sample characteristics and soxhlet extraction conditions). Alkanes from C_{11} to C_{30} were identified in the benzene leachables by interpretation of mass spectra data (Table 2). Also the following aromatics were identified. Peaks 1, 2, 3 are alkyl substituted benzenes; peaks 22 to 27 and 38, 39, and 42 and 53 have been identified as alkyl substituted naphthacenes. Alkyl substituted phenanthrenes (peaks 73, 74) and pyrenes (peaks 85, 86) were identified. Peak 67 has been tentatively identified as elemental sulfur.

GC/MS of TLC Fractions

A chromatographic trace of a standard PAH mixture and an example of a 0.6 to 0.8 R_f TLC fraction concentrate GC/MS injection are compared in Figure 2. This injection is equivalent to the benzene leachables from about 2.5 g of shale developed as described in Figure 3. Single ion mass spectrum reconstructions indicate the presence of three, four, and five ring aromatic

Hewlett-Packard gas chromatograph-mass spectrometer (HP 5985 GC/MS system)
10 meter glass capillary column coated with SP2100
Temperature programmed from 90° to 250° centigrade at 5°/min
(See Table 1 for sample and workup characterizations)

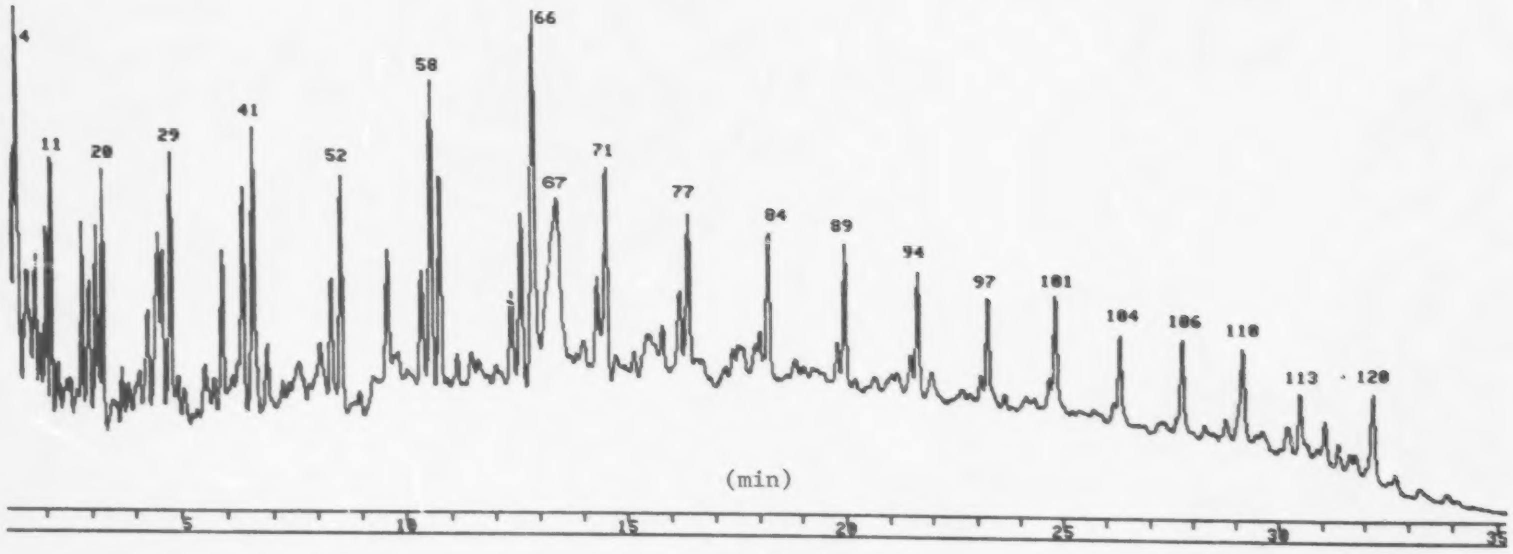

Figure 1. Gas Chromatography of Benzene Soxhlet Leachables.

Table 2. IDENTIFIED BENZENE LEACHABLES

Peak Number	Formula	Molecular Weight	Compound
1	$C_{10}H_{14}$	134	Benzene, di- or tri-alkyl substituted
2	$C_{10}H_{14}$	134	Benzene, di- or tri-alkyl substituted
3	$C_{11}H_{22}$	154	1-undecene
	and $C_{10}H_{14}$	134	Benzene, di- or tri-alkyl substituted
4	$C_{11}H_{24}$	156	Undecane
5	$C_{10}H_{12}$	132	Benzene, di-alkyl-alkenyl-substituted
7	$C_{11}H_{16}$	148	Benzene, alkyl substituted
8	$C_{10}H_{8}$	128	Naphthalene or azulene
9	$C_{11}H_{14}$	146	?
10	$C_{12}H_{24}$	168	1-dodecene
11	$C_{12}H_{26}$	170	Dodecane
12	$C_{13}H_{28}$	184	Undecane, dimethyl
16	$C_{11}H_{10}$	142	Naphthalene, methyl
17	$C_{11}H_{10}$	142	Naphthalene, methyl
18	$C_{13}H_{26}$	182	1-tridecene
20	$C_{13}H_{28}$	184	Tridecane
22	$C_{13}H_{18}$	174	Naphthacene, 1,2,3,4-tetra hydro-tri-alkyl substituted
23	$C_{12}H_{10}$	154	1,1'B,phenyl or acenaphthycene, 1,2-dihydro
25	$C_{12}H_{12}$	156	Naphthacene, mono- or di-alkyl substituted
26	$C_{12}H_{12}$	156	Naphthacene, mono- or di-alkyl substituted
27	$C_{12}H_{12}$	156	Naphthacene, mono- or di-alkyl substituted
28	$C_{14}H_{28}$	196	1-tetradecene
29	$C_{14}H_{30}$	198	Tetradecane
30	$C_{12}H_{12}$	156	Naphthacene, mono- or di-alkyl substituted
36	?	?	Alkane, substituted
37	?	?	Alkane, substituted
38	$C_{13}H_{14}$	170	Naphthacene, trimethyl substituted

Table 2. CONTINUED

Peak Number	Formula	Molecular Weight	Compound
39	$C_{13}H_{14}$	170	Naphthacene, trimethyl substituted
40	$C_{15}H_{30}$	210	1-pentadecene
41	$C_{15}H_{32}$	212	Pentadecane
42	$C_{13}H_{14}$	170	Naphthacene, trimethyl substituted
43	$C_{13}H_{14}$	170	Naphthacene, trimethyl substituted
44	$C_{13}H_{14}$	170	Naphthacene, trimethyl substituted
46	$C_{14}H_{16}$	184	Naphthacene, alkyl substituted
47	?	?	Alkane, substituted
48	?	?	Alkane, substituted
49	?	182	?
51	$C_{16}H_{32}$	224	1-hexadecene
52	$C_{16}H_{34}$	226	Hexadecane
53	$C_{14}H_{16}$	184	Naphthacene, alkyl substituted
55	?	?	Alkane, substituted
56	?	196	?
57	$C_{17}H_{34}$	238	1-heptadecene
58	$C_{17}H_{36}$	240	Heptadecane
59	$C_{19}H_{40}$	268	Alkane, substituted
60	?	?	Alkane, substituted
61	?	?	Alkane, substituted
63	$C_{13}H_{10}S$	198	Dibenzothiophene, methyl substituted
64	$C_{18}H_{36}$	252	1-octadecene
65	$C_{18}H_{40}$	254	Octadecane
66	?	?	Alkane, substituted
	and	192	Phenanthrene or anthracene, methyl substituted
67	S_8		Sulfur ?
70	$C_{19}H_{38}$	266	1-nonadecene
71	$C_{19}H_{40}$	268	Nonadecane
73	$C_{16}H_{14}$	206	Phenanthrene, dimethyl substituted
74	$C_{16}H_{14}$	206	Phenanthrene, dimethyl substituted

Table 2. CONTINUED

Peak Number	Formula	Molecular Weight	Compound
76	$C_{20}H_{40}$	280	1-eicosene
77	$C_{20}H_{42}$	282	Eicosane
83	$C_{21}H_{42}$	294	1-heneicosene
84	$C_{21}H_{44}$	296	Heneicosane
85	$C_{17}H_{12}$	216	Pyrene, methyl substituted or 11H-benzo[a]fluorene
86	$C_{17}H_{12}$	216	Pyrene, methyl substituted
88	$C_{22}H_{44}$	308	1-docosene
89	$C_{22}H_{46}$	310	Docosane
93	$C_{23}H_{46}$	322	1-tricosene
94	$C_{23}H_{48}$	324	Tricosane
96	$C_{24}H_{48}$	336	1-tetracosene
97	$C_{24}H_{50}$	338	Tetracosane
100	$C_{25}H_{50}$	350	1-pentacosene
101	$C_{25}H_{52}$	352	Pentacosane
103	$C_{26}H_{52}$	364	1-hexcosene
104	$C_{26}H_{54}$	366	Hexcosane
105	$C_{27}H_{54}$	378	1-heptacosene
106	$C_{27}H_{56}$	380	Heptacosane
107	?	253	?
108	?	217	?
109	$C_{28}H_{56}$	392	1-octacosene
110	$C_{28}H_{58}$	394	Octacosane
112	?	217	?
113	$C_{29}H_{60}$	408	Nonacosane
114	?	217	?
115	?	217	?
117	?	217	?
119	$C_{30}H_{62}$	422	?

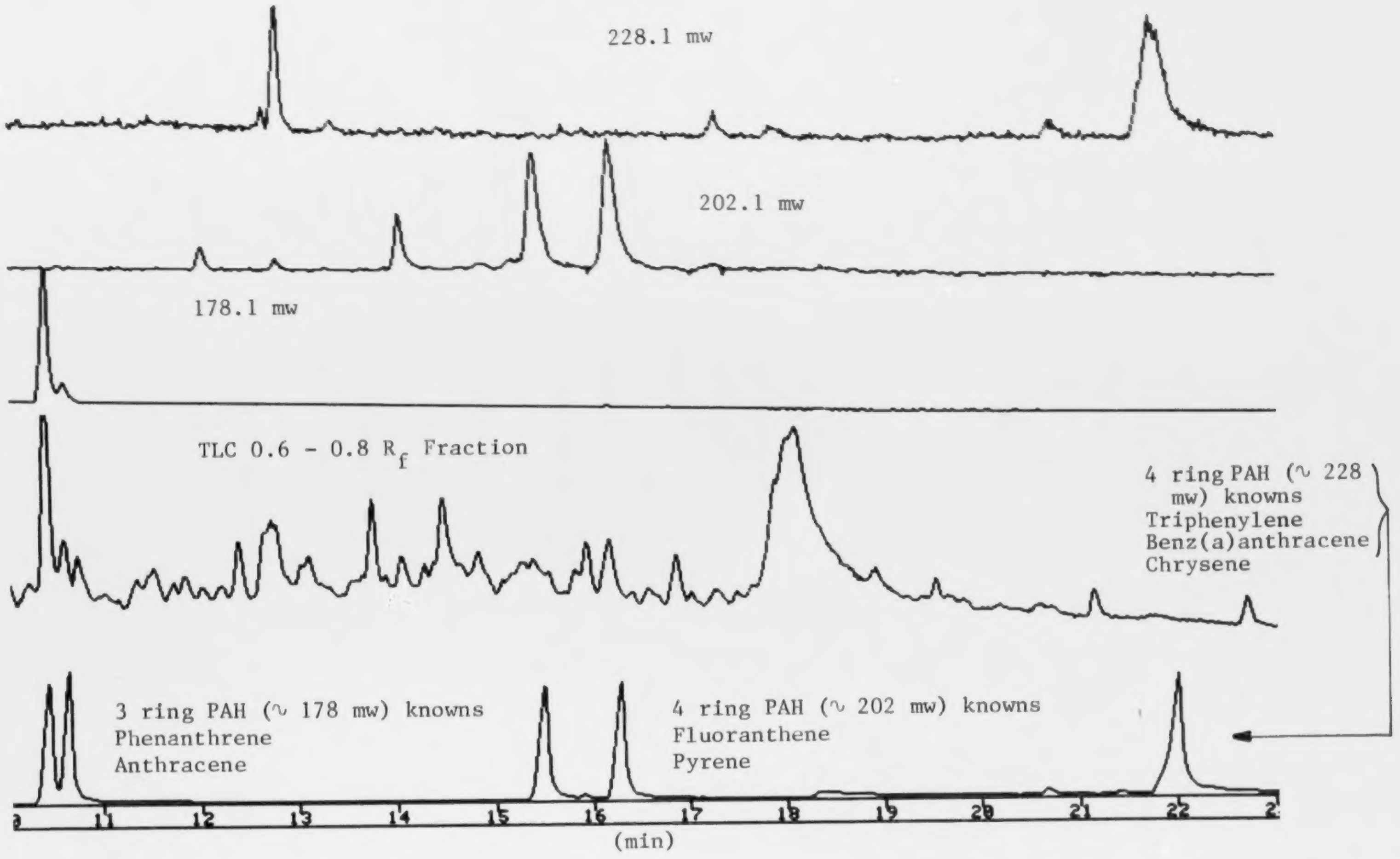

Figure 2. Gas chromatography comparison of a TLC 0.6-0.8 fraction with known PAH.

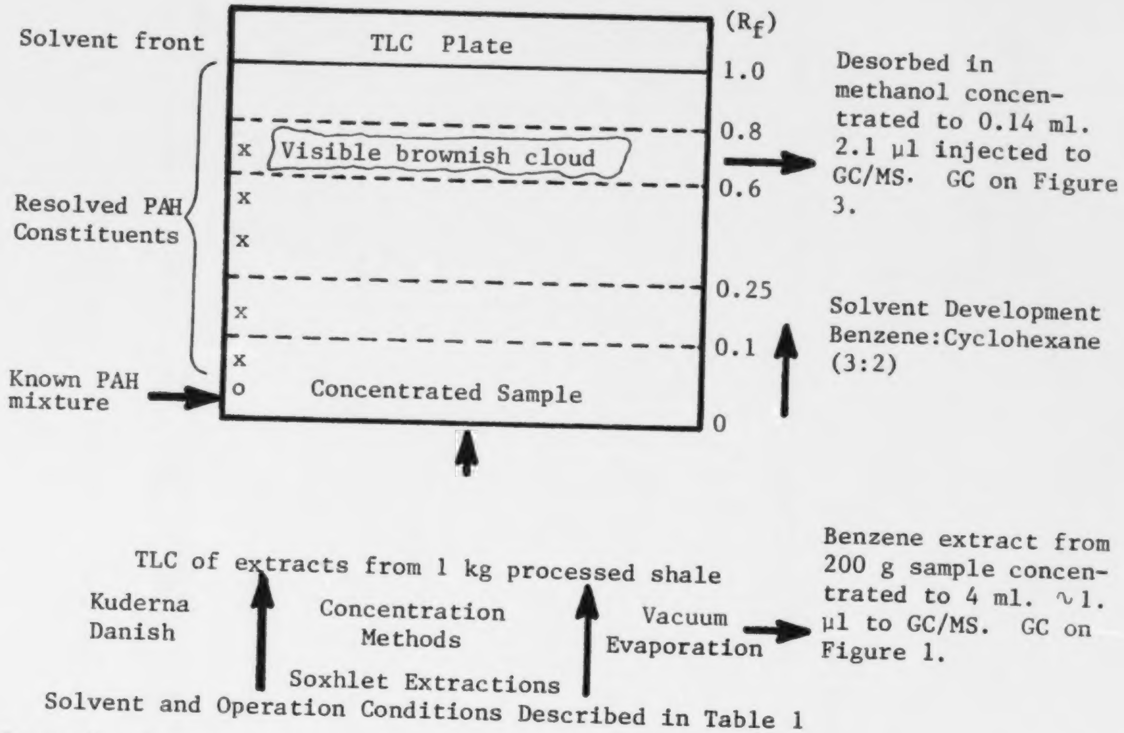
Solvent front
TLC Plate
(Rf)
1.0
0.8
x
Visible brownish cloud
0.6
x
x
0.25
x
0.1
x
o
Concentrated Sample
0
Resolved PAH Constituents
Known PAH mixture
Desorbed in methanol concentrated to 0.14 ml. 2.1 µl injected to GC/MS. GC on Figure 3.
Solvent Development Benzene:Cyclohexane (3:2)
TLC of extracts from 1 kg processed shale
Kuderna Danish
Concentration Methods
Vacuum Evaporation
Benzene extract from 200 g sample concentrated to 4 ml. ∿1. µl to GC/MS. GC on Figure 1.
Soxhlet Extractions
Solvent and Operation Conditions Described in Table 1

Figure 3. Summary of organic extraction regime.

Table 3. SUMMARY OF PAHs IDENTIFIED IN TLC 0.6 to 0.8 R_f FRACTION

Number Aromatic Rings	GC/MS Identified Compound	Molecular Wt.	Formula	Retention Time (min)
3	anthracene	178.1	$C_{14}H_{10}$	10.2
3	phenanthrene	178.1	$C_{14}H_{10}$	10.4
4	pyrene	202.1	$C_{16}H_{10}$	15.6
4	fluoranthene	202.1	$C_{16}H_{10}$	16.3
4	benzo(a)anthracene chrysene triphenylene benzo(c)phenanthrene	228.1	$C_{18}H_{12}$	22.0

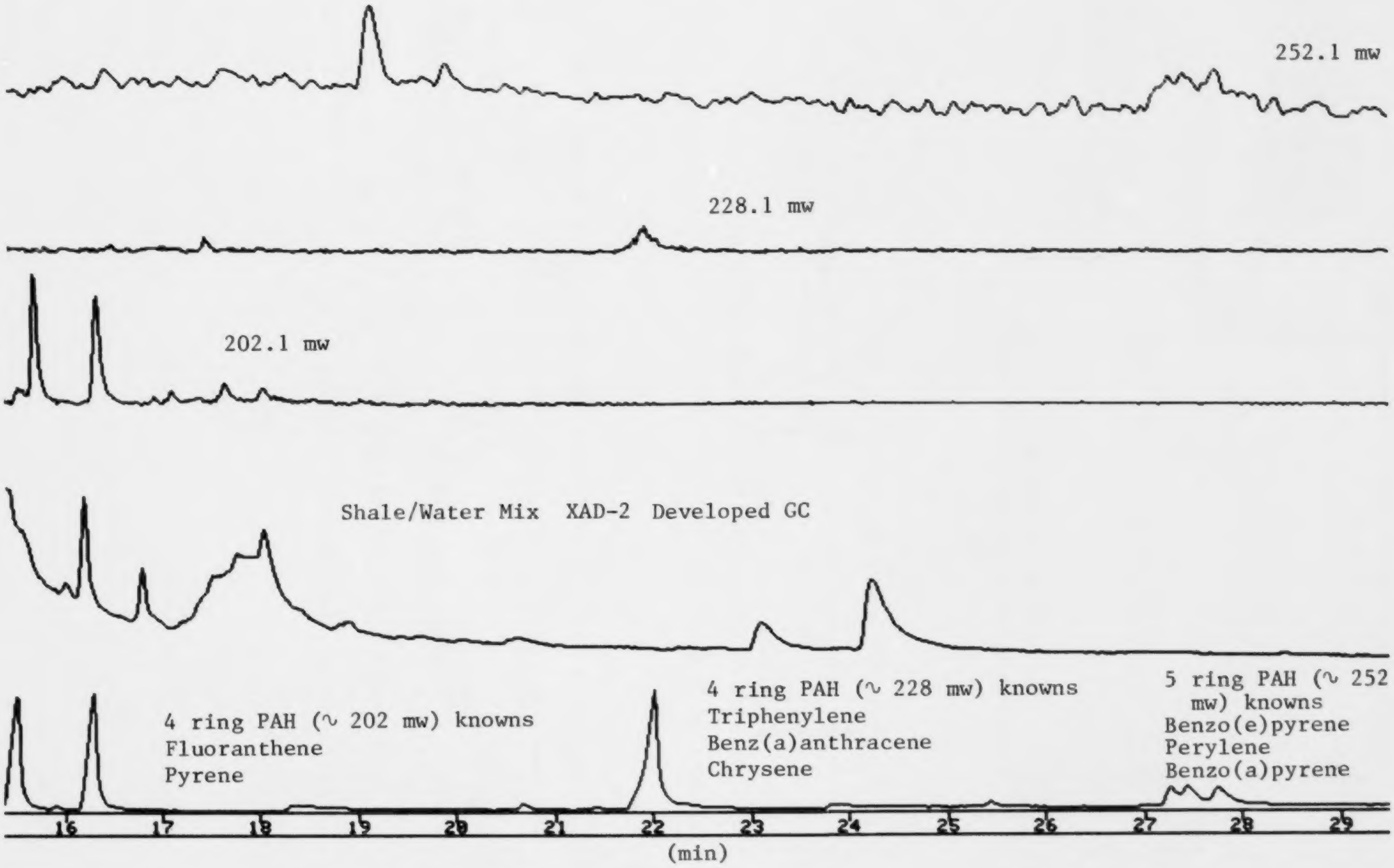

Figure 4. Gas chromatography comparison of a XAD-2 developed water extract with known PAH.

hydrocarbons. From mass spectrum information the ring compounds are further identified as shown in Table 3. The four ring 228 mw PAH, benz(a)anthracene, chrysene and triphenylene, could not be separately identified by the GD/MS computer library. The mass spectrum of benzo(c)phenanthrene was identified. Five ring aromatics (benz a and e pyrenes and perylene) were indicated by GC retention time comparison with gas chromatography of the standard PAH mixture. However, insufficient concentrations of the five ring aromatics were present above background to allow identification of mass spectra.

GC/MS of Water Extracts

A portion of a GC trace of a XAD-2 developed processed shale water mix is compared to the PAH standard in Figure 4. Three ring 178 mw and four ring 202 molecular weight PAH were indicated by retention time and identified by comparison of GC/MS library mass spectra. Only a weak presence of four ring 228 mw PAH is indicated by single ion reconstruction GC/MS traces. The five ring 252 mw benzo(e)pyrene, perylene and benzo(a)pyrene seem to be extractable by the shale/water mixing technique. However, the concentration above background of the four and five ring aromatics were not high enough to allow comparison of mass spectra. The larger peaks shown on this GC trace are believed to be phthalic esters.

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Table A1. SUMMARY OF SELECTED OIL SHALE INVESTIGATIONS OF ORGANICS

Source	Samples Analyzed	Identification Methods and/or GC Columns and Conditions	Procedure Keywords and Other Comments
Chong et al. 76	Oil shale thermally degraded with $CO-H_2O$	50' SE - 30 SCOT 100^o-275^o @ 5^o/min	Extracted with benzene and methanol LC IRA-904 anion, A-15 cation, $FeCl_3$— clay IRA-904 anion, silica gel, 5Å molecular sieve
Cummins et al. 72 and 74	Raw shales in situ simulation columns	50' SE - 30 capillary column	4.7 kg stirred in 6 ℓ benzene 1/2 days + 10 min ultrasonic → 7.5% organics extracted LC alumina of pentane solubles LC silical gel and 5Å molecular sieve → alkanes
Gallegos 73	Green River shale	200' x 0.02" Dexsil coated capillary GC/MS	Crushed 2-3 mm, soxhlet extraction for one week 50:50 benzene:methanol TIM ? Chromatography
Jacobson et al. 74	Raw shales Utah Wyoming Colorado	1/8" od 10' SS 150/200 mesh Poropak Q He 50-180^oC	Pyrolysis procedure, retorting study
Kwan et al. 78	Spent and raw shales +	GC/MS and HPLC	Spent shale ground to <100 mesh soxhlet extracted 48 hrs benzene, roto evaporation LC-alumina benzene-methanol fractions
Maase and Adams 79 and Dickson and Porcella 79	Processed shales	10 m glass capillary column with SP2100 90-250^oC @ 5^o/min	Soxhlet extraction 3 days with benzene then methanol extraction → Ames test Flash evaporation and Kuderna Danish TLC

Table A1. CONTINUED

Source	Samples Analyzed	Identification Methods and/or GC Columns and Conditions	Procedure Keywords and Other Comments
Robinson and Cook 71	Oil shale, raw	IR	Crushed, C_6H_{12} soxhlet 24 hrs L/L ultrasonic, flash evaporation (10 torr) TAR Problem molecular sieves other work with pentane
Robinson and Cook 73	Raw shale Wyoming	Not reported	<8 mesh → <100 mesh 24 hr. soxhlet with cyclohexane, elution chromatography and molecular sieves +++
Saxby in Yen 76b Chapter 6	Shale kerogen	Not reported	Soxhlet extraction benzene:methanol Acid/Basic fractionation TAR and moisture problems Identification $C_{40}H_{80}$
Schmidt-Collerus 74	Spent shale	50' Corasil SCOT 100^{o}-$300^{o}C$	Benzene, 6 day soxhlet extraction Flash evaporation/Kuderna Danish TLC identification/separation Show PAH mobility with polar solvents
Thomas and Lorenz 70	Raw shales	Not reported	Centrifical separation macro characteristics C, N, S, Fe, H with/without TAR problem
Yen 76	Shale bitumen kerogen	Not reported	Benzene soxhlet extraction, fluorescence, GC, HPLC, UV macro element characterization kerogen model, geological origin ? , much more

Table A2. SELECTED INVESTIGATIONS OF PRODUCTS AND WASTES DERIVED FROM SHALES, TAR SAND, COAL, AND HIGH BOILING CRUDE OIL DISTILLATES

Source	Samples Analyzed	Identification Methods and/or GC Columns and Conditions	Procedure Keywords and Other Comments
Bunger 77	Tar Sand Bitumens	NMR, MS, IR	Review of methods of analysis! Problems with flash evaporation macro characterization C, H, N, S inorganics!
Callen et al. 77	Oils (related)	NMR, IR	LC: n-Pentane, benzene, THF Pyridine, macro characterization O, N, S, C Heteroatom concentrations
C.-h. Ho et al. 79	Shale oil 150 ton Laramie Retort	1/8" x 20' 3% Dexsil 400 on 100/120 mesh Chromosorb 750	Centrifuge separation water/oil/emulsion Acid/Base LL extractions LC Sephadex LH-20, Silicic Acid, Basic Alumina Neutral Aza-arenes suggested
Clark et al. 77	Shale oil COED Syncrude	3% Dexsil packed 400 column	Benzene → Pyridine extraction Flash evaporation problems LC Florisil, Alumina, Sephadex DMSO, Cyclohexane, H_2O fractions
Fruchter et al. 77	Shale oil solvent refined coal materials	6' 3% SP2100 120° - 250°C	Isooctane/HCl/NaOH DMSO fractionations Irradiation of samples for standard also inorganics
Greinke and Lewis 75	Coal and petroleum pitch volatiles	GC, MS, UV 1/8" x 10' SS 3% Dexsil 300 on Chromosorb G	Distillation of petroleum pitch collected volatiles soxhlet extracted with cyclohexane 3-5 ring PAH content estimated
Guerin 77	Crude oils Coal oils Shale oils	USBM-API procedure	Comparison of PAH from energy sources, combustion products, conversion products and other processing wastes +
Jones et al. 77	Oils from coal and shale	GC/MS 3% Dexsil 400 70-320°C @ 4°/min	LC Sephadex LH-20 elution of PAH with 2 ℓ THF and 2 ℓ ethanol

Table A2. CONTINUED

Source	Samples Analyzed	Identification Methods and/or GC Columns and Conditions	Procedure Keywords and Other Comments
Jones in Coomes 78	Shale oil and related fuels	6' 1% OV-101 100-340^{o} @ 4^{o}/min	LC Silica Gel Petroleum ether and CH_2Cl_2 methanol fractions
Pellizzari 78	Energy related wastes and effluents	100 m glass SCOT OV-101 20-240^{o}C @ 4^{o}/min; 50 m glass SCOT, others	Liquid and solid effluents from oil shale, coal gasification and coal liquefaction processes, coal fired power plants and oil refineries ++!
Rubin et al. 76	Crude oils from coal	Fractionation for biological testing	L/L Acid/Base extractions LC florisil of neutral fraction eluted with hexane, benzene, ether, methanol
Schweighardt and Thomas 78	Coal derived products	-	Liquid nitrogen saponification N-Pentane/benzene/THF
Selucky et al. 77	Bitumen	HPLC	LC N-Pentane/Benzene molecular sieve (5Å) thiourea
Sharkey et al. 76	Coal, ashes Shale oils Ferroalloy	"high resolution MS" 300^{o}C 10^{-6} torr	Analysis of PAH in coal, coal ash, fly ash, and other fuel and emission samples
Schiller and Mathiason 77	Oils, Tar Sand and Coal derived	1/8" x 10' SS 5% SE - 30 on Chromosorb W	Mixed tar with 2-3g Al_2O_3(N)LC Alumina CCl_3H, tetrahydrafuran/hexane/toluene/chloroform THF/ethanol fractions
Uden et al. 79	TOSCO II Shale Oil Acids and Bases	GC/IR 100' x 0.03" SCOT FFAP on Chromosorb R	L/L Acid Base extractions substituted pyridines and quinolines and phenols identified

Table A3. SELECTED INVESTIGATIONS OF AIR CONCENTRATIONS OF PAH

Source	Samples Analyzed	Identification Methods and/or GC Columns and Conditions	Procedure Keywords and Other Comments
Cautreels and Cauwenberghe 77	Aerosol extracts	3 m 4% Dexsil-300 120-280^{o}C @ 4^{o}/min	Soxhlet extraction 4 hrs benzene, 4 hrs methanol redissolved in ether, washed in water Acid/Base fractions
Daisey and Leyko 79	Air filters	3.18 mm x 3.66 m SS with 6% Dexsil 300 on 80/100 Chromosorb W (HP)	Soxhlet extraction with cyclohexane TLC acetylated cellulose ; propanol-acetone-water (2:1:1)
Hill et al. 77	Air filters	10' x 2 mm glass packing coated with Carbowax 20 100-240 @ 4^{o}/min	Soxhlet extraction with methanol redissolved in cyclohexane
Lee and Novotny 76	Air filters	19 m x 0.26 mm glass capillary SE-52	Column study 180 cm x 0.32 cm od stainless steel column 3% Dexsil 300 on 80/100 mesh Chromosorb W
Natusch and Tomkins 78	Air filters	1/4" od x 6' glass 1.5-3% SP2100 80/100 mesh + others	Dimethyl sulfoxide soxhlet extraction n-pentane, n-heptane isooctane, n-hexane fractions
Pierce and Katz 75	Aerosols	Not reported	Benzene soxhlet extraction TLC preseparation polycyclic Quinones identified
Pitts et al. 78	Air filters	-	TLC solvent toluene: CH_2Cl_2:Methanol 25:1:1 Silica gel plates deadsorption in methanol → Ames test

Table A4. SELECTED INVESTIGATIONS CONCERNING PAH WATER CONCENTRATIONS

Source	Samples Analyzed	Identification Methods and/or GC Columns and Conditions	Procedure Keywords and Other Comments
Acheson et al. 76	Synthetic and river water	TLC GLC	Ultra-Turrax resin → CH_2Cl_2 extraction efficiency study variables suspended solids, initial concentration
Adams et al. 77	Water with knowns	Chromosorb 101 and 102 XAD 2 and 4 Tenex - GC and Poropak	Comparison of sorbent resins properties and efficiencies for C_6 - C_{13} alkanes and 1 to 4 ring PAH
Chriswell et al. 77	Water with known PAH	GC 3 mm x 1.8 m SS column packed with 5% OV-1 on 100/120 mesh Chromosorb WAW 75-250°C @ 8°/min	Study of XAD-2 and carbon adsorption recovery of trace organic from water
Dunlap et al. 77	Groundwater	XAD-2 resin extraction	Sampling and extraction study of groundwaters
EPA 77	Industrial wastewater	L/L extraction CH_2Cl_2 H/HO	Sampling and analysis procedures for screening of industrial for priority pollutants
Junk et al. 74	Water	XAD-2 resin extraction	Study of removal of trace organics from water

Table A4. CONTINUED

Source	Samples Analyzed	Identification Methods and/or GC Columns and Conditions	Procedure Keywords and Other Comments
Kwan et al. 77	Shale retort water	IR, UV, GC HPLC	L/L extractions with ether for 2 weeks Acid/Neutral/Basic fractions
May et al. 78	Water with PAH standards	XAD-2 resin extraction	Study of PAH water solubilities Naphthalene → Chrysene
Spath 72	Ohio River water	GC 1/8" x 6' SS 10% silicone grease on Gas Chrom Q	Background study and results of chlorination of PAHs Naphthalene - Pyrene
Stepan and Smith 77	Water with knowns	2 mm x 3.5 m glass column 3% SE-30	XAD-2 and 7 extraction efficiency study variable flowrate, pH, temperature
Webb 75	Water with knowns	XAD resins urethane foam solvent extraction	Comparison of isolation methods for ∿ C_6 alkanes and 1 to 4 ring PAH

Table A5. SELECTED INVESTIGATIONS OF PAH CONTENT IN OTHER ENVIRONMENTAL SAMPLES

Source	Samples Analyzed	Identification Methods and/or GC Columns and Conditions	Procedure Keywords and Other Comments
Brown et al. 78	Marine sediments	30 m x 0.25 mm Glass capillary SE 54 WCOT col.	Benzene/methanol soxhlet extractions; LC on silica gel
Farrington 78	Near offshore sediments	Glass capillary	"EPA mussel watch" pyrene and chrysene identified
Giger and Blumer 74	Sediments	UV, MS, GC	Soxhlet extractions methanol and benzene LC-Sephadex LH-20, Silica gel, Alumina removal of H_2O, S; UV estimation of PAH contents through coronene
John and Nickless 77	Sediments	4 mm x 3' with 5% Dexsil 300 on 60/80 mesh chromosorb W	Na_2SO_4 water removal, soxhlet extraction CH_2Cl_2 LC x 2 then TLC
Lao et al. 75	Sludges, tar, soot, air	0.125" x 12' SS packed with 6% Dexsil 300, 400, or 410 on 80/100 mesh Chromosorb W HP	Cyclohexane soxhlet extraction 24 hrs; or separatory funnel 24 hrs CH_2Cl_2
Lee and Hites 76	Carbon black	11 m x 0.26 mm Glass capillary SE-52	Soxhlet extraction CH_2Cl_2 for 18 hrs
Pancirov et al. 78	Wastewater refinery sediments	1/8" x 10' 2% SE 30 on Chromosorb G He 40 ml/min 175-300° @ 4°/min	C^{14} as a standard CH_2Cl_2 soxhlet extraction LC on alumina elutions isooctane to DMSO

POLAR CONSTITUENTS OF A SHALE OIL: COMPARATIVE COMPOSITION WITH OTHER FOSSIL-DERIVED LIQUIDS[*]

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Historically, polar compounds in petroleum crudes and products have been of interest to chemists and engineers because some categories of these compounds have a commercial value if they can be separated, while others have detrimental effects on refinery processes and end uses of the product.[1] Acidic and basic components can provide either larger benefits or worse problems in fuels derived from coal or shale, because they are generally present in higher quantities than in petroleum crudes. In natural crudes, acids and bases comprise usually not more than 1% to 2% each,[1] while in the synthetic crudes they may total as much as 10%, as will be seen below. In recent years, environmental concerns have added another dimension to the analysis of fossil fuels. These concerns regarding both the production and end uses of fossil fuels have required increasing efforts to examine all aspects of fossil fuel technology for their potential effects on living systems. For many years this effort was devoted mainly to the study of the polycyclic aromatic hydrocarbon fraction, constituents of which are known to have tumorigenic effects, but recent studies have shown that, as measured by the Ames test for mutagenicity, some of the polar classes of compounds have as large, if not a larger, biological effect.[2]

The use of strong acids and bases for the separation of bases and acids respectively from crudes and refinery products has been accepted practice virtually since the beginnings of the modern petroleum industry.[1] Although other separations methods, such as the Bureau of Mines-API procedure in which ion exchange resins are used, have been developed,[3] acid/base extractions seem to be generally adaptable to a wide variety of materials.[4-8] Another recent separations procedure uses Sephadex LH-20 gel as a support for the partitioning of polar and nonpolar compounds into a hexane/aqueous methanol solvent system.[9,10] The polar fraction can then be subfractionated into its acidic and basic components.

In our work we have chosen to follow both the acid/base and the LH-20 procedures as well as combinations of the two. This acid/base fractionation scheme[7] has been adapted from that described by Swain et al.[6] Modifications of the early acid/base separations methods have proven applicable to a range of materials from Cincinnati tap water[4] to fungicides for rubber trees in Malaya,[5] and including shale oil.[8] The method involves extractions from ether solutions of the sample initially with 1 N hydrochloric acid and 1 N sodium hydroxide followed by extractions with ether at pH 6, 1 and 11. Water soluble acids and bases are recovered as are the various insoluble materials. A comparison of the quantities of acids and bases recovered from several materials is shown in Table 1, and one can see that they vary greatly from material to material. Reproducibility of the fractionation is good as is shown in Table 2 for three of the polar fractions in shale oil. These data are in chronological order and cover a period of about two and a half years. It can be seen that except for the weak acids, there is no difference between the early and later results. Recent data from samples run simultaneously in triplicate show the same order of precision. Distribution can be checked by using radioactive tracers if one desires. We have done independent studies with an aqueous solution of standard compounds and found that distribution among the polar fractions, plus the neutral, is as we had expected. For quality assurance, we periodically fractionate one shale oil of which we have an ample quantity and which apparently has not changed much in chemical class composition in three years. This oil has been selected as a standard oil by the National Bureau of Standards.

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The full fractionation scheme using Sephadex LH-20 has been described by Jones et al.[10] The polar constitutents are found mainly in the hydrophilic and H-bonding fractions. Once the lipophilic fraction has been completely eluted with hexane, the hydrophilic can be eluted with the aqueous methanol solution by reversing the flow. Since this is a lengthy procedure, we prefer to elute the hydrophilic with acetone, although this has the disadvantage of shrinking the gel and necessitating repacking the column. The gravimetric yields for the hydrophilic and H-bonding fractions of several materials is shown in Table 3, and again one can see the variability among materials. The distribution between lipophilic and hydrophilic fractions is very reproducible as shown by the data in Table 4. Recovery of the hydrophilic fraction is very nearly the same regardless of the scale of the operation, as is the precision. The difference in total recovery was caused by the fact that in the large scale work, the volatiles and insolubles were removed prior to chromatography, while they were not in the small scale work. About two years elapsed between these two studies. As with the acid/base procedure, quality assurance can be maintained by periodically chromatographing radio-tracers, a synthetic mixture or a control oil.

Fractions are defined by the operation used for their isolation, rather than strictly by composition because of the solubility and other problems that cause cross contamination among the various fractions. As we see below, the hydrophilic fraction contains not only acid and base but also neutral components. The neutral fraction of shale oil contains about 5% hydrophilic material when it is chromatographed on LH-20, while the lipophilic fraction was found to contain about 7% ether soluble base fraction when it was subjected to an acid/base extraction. This is the same proportion as found in the whole oil.

TABLE 1. COMPARATIVE ACID AND BASE COMPOSITION OF FOSSIL FUEL PRODUCT OILS

Fraction	Weight Percent of Original Sample			
	Shale Oil	Coal Oil A	Coal Oil B	Mixed Crude Oils
Weak Acids, Ether Sol.	1.1	1.6	4.7	0.3
Strong Acids, Ether Sol	0.3	1.3	0.7	0.4
Acid, Water Sol.	0.6	1.0	0.4	0.1
Bases, Ether Sol.	7.0	2.2	2.0	0.2
Bases, Water Sol.	0.4	0.4	0.3	0.5
TOTAL	9.4	6.5	8.1	1.5

TABLE 2. REPRODUCIBILITY OF FRACTIONATION FOR ACID AND BASE FRACTIONS OF SHALE OIL

Date	Weight Percent of Original Sample		
	Weak Acid	Strong Acid	Base
2/20/76	1.33	0.45	6.87
3/15/76	1.23	0.26	7.11
7/12/76	1.33	0.20	7.01
10/25/76	0.74	0.25	6.86
10/17/78	0.88	0.42	7.22
10/17/78	0.67	0.25	7.18
Ave.	1.09	0.31	7.04
RSD, %	29.0	34.0	2.0
Wt. range, g	5-100		

TABLE 3. COMPARISON OF POLAR FRACTIONS OF FOSSIL FUEL OILS AFTER GEL PARTITION CHROMATOGRAPHY

Sample	Weight Percent of Original Sample	
	Hydrophilic	H-Bond
Shale Oil	7.0	5.2
Coal Oil A	3.4	8.2
Coal Oil B	10.9	5.7
Coal Oil C	18.5	0.0
Crude Oils	0.8	14.9

TABLE 4. REPRODUCIBILITY OF LIPOPHILIC/HYDROPHILIC DISTRIBUTION BY GEL PARTITION CHROMATOGRAPHY

A. Small scale procedure

Wt. Range, g: 0.05-1.0
Column Vol., ml: 11
n: 24

Recovery, %		
Lipophilic	Hydrophilic	Total
87.6 ± 4%	6.8 ± 21%	94.2 ± 3%

B. Large scale procedure*

Wt. Range, g: 17-300
Column Vol., ml: 2000
n: 5

Recovery, %		
Lipophilic	Hydrophilic	Total
93.4 ± 1.5%	6.0 ± 17%	99.4 ± 1.5%

*Calculated from data in Reference 10.

The hydrophilic fraction is a very complex mixture, so it was subsequently subfractionated by an acid/base procedure. The flow diagram of this separation is shown in Figure 1. It is essentially the same as described previously,[7] except that methylene chloride was used instead of ether and potassium rather than sodium hydroxide. Distribution of the subfractions for several fuel oils is shown in Table 5. The shale oil fraction can be seen to contain more base and strong acid materials than those from the coal-derived products, which in turn, contain more phenolic matter. A considerable portion of these hydrophilic fractions appeared to be nonpolar in nature when confronted with strong acid and base. This "neutral" portion was then subfractionated by sbsorption chromotography on alumina. Distribution of the neutral subfractions are shown in Table 6. Very little, if any, material is eluted with cyclohexane and benzene, so there is an almost complete lack of saturates and aromatics. Since the bulk of the material is eluted with methanol, indications are that these compounds have strong absorptive capabilities.

These methanol eluted subfractions have been examined by elemental analysis, nuclear magnetic resonance spectroscopy and infrared absorption spectrophotometry. These materials are essentially nonvolatile. Gas chromatography of these and similar samples on Dexsil 400 packed columns at temperatures as high as 320°C reveal no significant peaks, so GC-mass spectroscopy could not be used for characterization studies. Direct probe studies of similar subfractions produced such complex mass spectra that no useful information could be acquired.

Results of the elemental analyses are presented in Table 7. Carbon and hydrogen were determined by standard combustion train analysis, nitrogen by the Kjeldahl procedure, sulfur by the Leco sulfur analyzer and oxygen by difference. Ratios of the other elements to carbon are shown in Table 8, as are postulated empirical formulae of the average compounds normalized to one nitrogen atom per molecule and molecular weights based on these formulae. The low hydrogen to carbon ratios indicate that the carbon residues are more aromatic than aliphatic in nature. It must be recognized that even though these subfractions comprise only a small portion of the original sample, they are still complex mixtures. The shale oil subfraction is about 4% of the original.

The proton NMR spectrum of the shale oil subfraction is shown in Figure 2, and for a coal product in Figure 3. Hydrogen data are summarized in Table 9. Values in the first column are methyl group absorptions γ and further from the aromatic ring. These values are about the same for each sample. Values in the 1.0 to 1.9 δ range correspond to CH_2 and CH protons β and further from the aromatic ring or activating group. Since these values are larger than those in the 0.5 to 1.0 δ range, they indicate average chains of medium length. The 1.90 to 3.50 δ region indicate hydrogen α to an aromatic ring, and the range in values show variations of substituents on the aromatic ring. Values in the last two columns are for noncondensed ring aromatics and condensed ring aromatics, respectively, while the 3.50 to 4.50 δ and 4.50 to 6.0 δ values are characertistic of protons influence by functional groups, in the former range by groups that may contain oxygen and/or

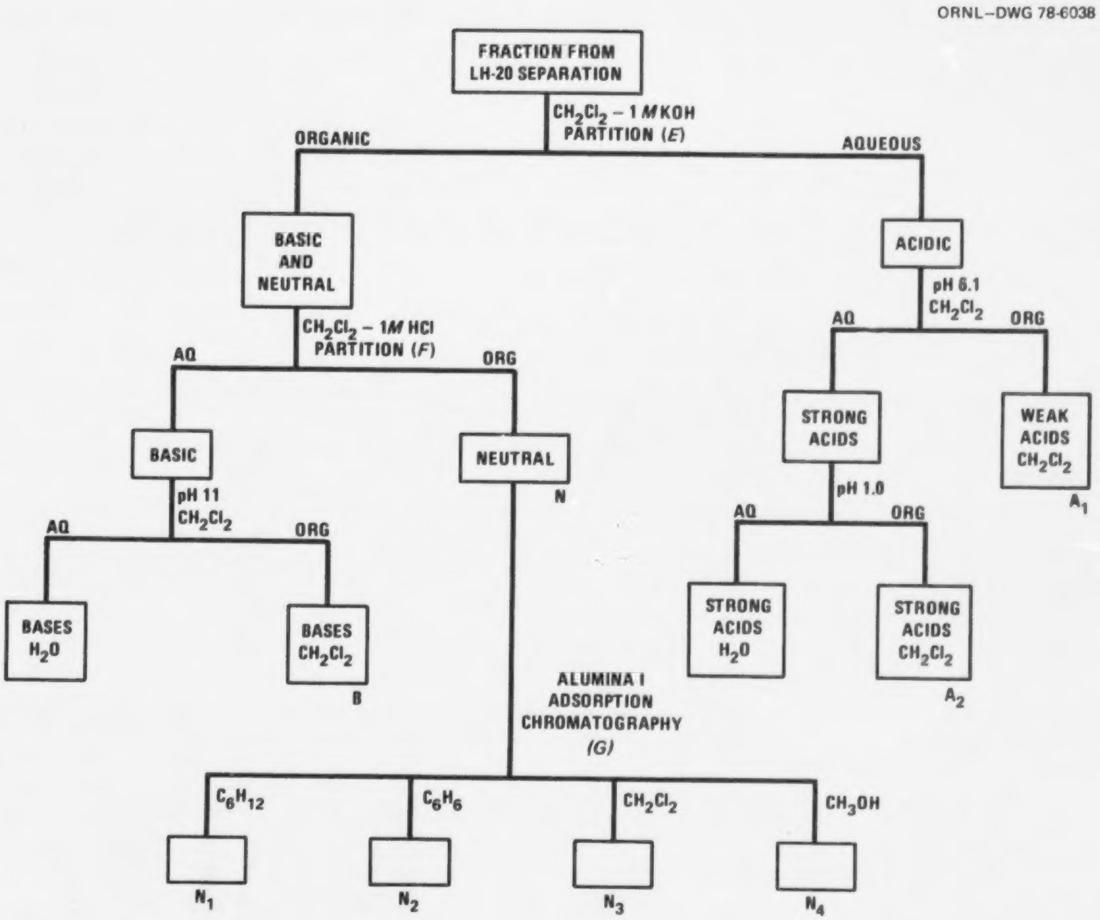

Figure 1. Flow Diagram for Subfractionation of Gel Partition Chromatography Fractions.

TABLE 5. DISTRIBUTION OF SUBFRACTIONS OF THE HYDROPHILIC PORTION OF FOSSIL FUEL OILS

Sample	Weight Percent of Hydrophilic Fraction				
	Weak Acid	Strong Acid	Base	Neutral	Total
Shale Oil	11.2	1.7	10.8	64.0	87.7
Coal Oil A	20.2	0.4	2.0	57.7	80.3
Coal Oil B	36.7	0.5	3.4	52.4	93.0
Coal Oil C	44.6	0.0	1.9	37.8	84.3
Crude Oils	3.2	0.7	4.2	79.9	88.0

TABLE 6. DISTRIBUTION OF THE NEUTRAL SUBFRACTION OF THE HYDROPHILIC PORTION OF FOSSIL FUEL OILS

Sample	Weight Percent of Neutral Subfraction				
	C_6H_{12}	C_6H_6	CH_2Cl_2	CH_3OH	Total
Shale Oil	0.3	1.0	0.8	85.1	87.2
Coal Oil A	0.0	1.4	3.4	71.9	76.7
Coal Oil B	1.1	0.9	1.1	81.3	84.4
Coal Oil C	0.6	1.2	0.0	98.2	100.0
Crude Oils	0.9	0.9	3.5	71.2	76.5

TABLE 7. ELEMENTAL ANALYSIS OF FOSSIL FUEL OILS SUBFRACTION

Sample	Weight Percent of Methanol Subfraction				
	C	H	N	S	O*
Shale Oil	75.3	7.76	5.18	1.42	10.34
Coal Oil A	81.3	8.00	3.10	0.17	4.60
Coal Oil B	81.7	7.78	1.86	0.61	8.05
Coal Oil C	79.5	7.70	1.86	0.21	10.73
Crude Oils	75.1	8.32	1.99	5.21	9.38

*By difference.

TABLE 8. ATOMIC RATIO OF OTHER ELEMENTS TO CARBON IN METHANOL SUBFRACTION

Sample	Ratio	H/C	N/C	S/C	O/C
Shale Oil		1.23	0.059	0.007	0.103
Coal Oil A		1.17	0.033	0.001	0.042
Coal Oil B		1.13	0.020	0.003	0.074
Coal Oil C		1.15	0.020	0.001	0.101
Crude Oils		1.32	0.023	0.026	0.094

Postulated Empirical Formula

Sample	Formula	MW
Shale Oil	$C_{17}H_{21}N_1O_2$	MW = 271
Coal Oil A	$C_{31}H_{36}N_1O_1$	438
Coal Oil B	$C_{51}H_{59}N_1O_4$	749
Coal Oil C	$C_{50}H_{58}N_1O_5$	752
Crude Oils	$C_{44}H_{58}N_1O_4$	664

TABLE 9. DISTRIBUTION OF HYDROGEN TYPES BY NMR IN METHANOL SUBRFACTION

Sample	Chemical Shift						
	0.5- 1.0 δ	1.0- 1.90 δ	1.90- 3.50 δ	3.50- 4.50 δ	4.50- 6.0 δ	6.0- 7.15 δ	7.15- 8.25 δ
	Percent of Hydrogen						
Shale Oil	13	37	37	-	-	5	8
Coal Oil A	10	26	31	1	7	17	8
Coal Oil B	11	26	26	-	5	21	11
Coal Oil C	11	32	19	4	3	16	16
Crude Oils	14	40	31	-	-	8	8

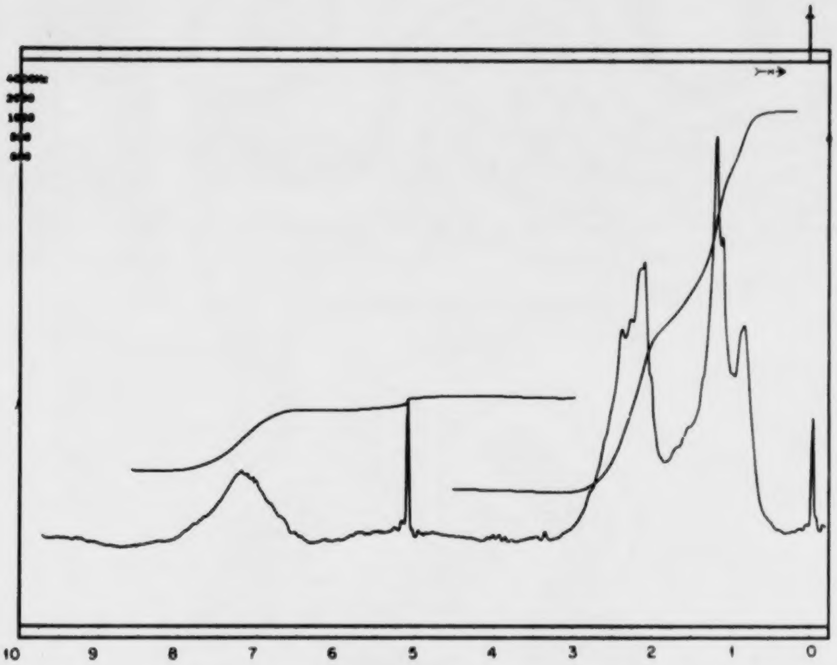

Figure 2. Proton NMR Spectrum of Methanol Subfraction of Shale Oil.

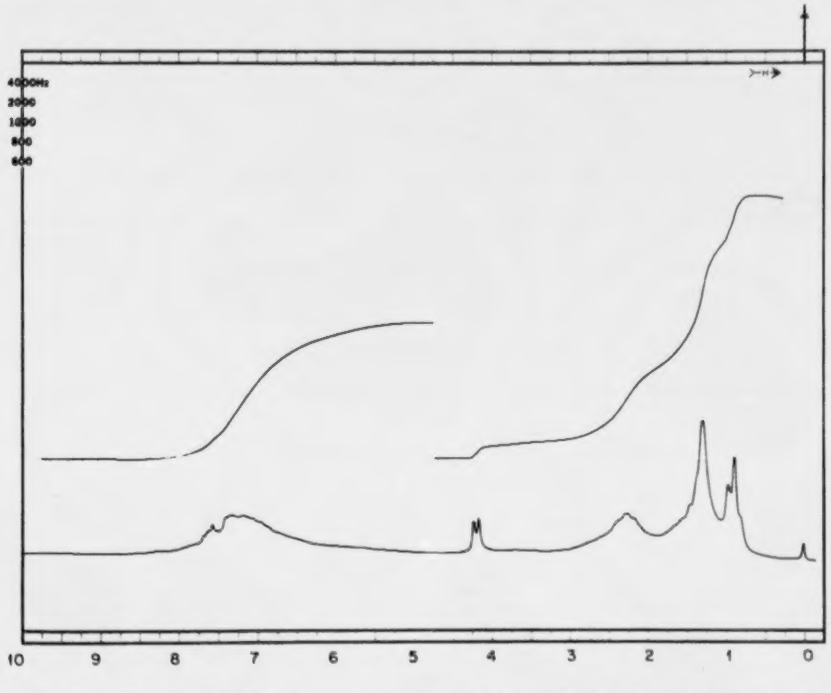

Figure 3. Proton NMR Spectrum of Methanol Subfraction of Coal Oil C.

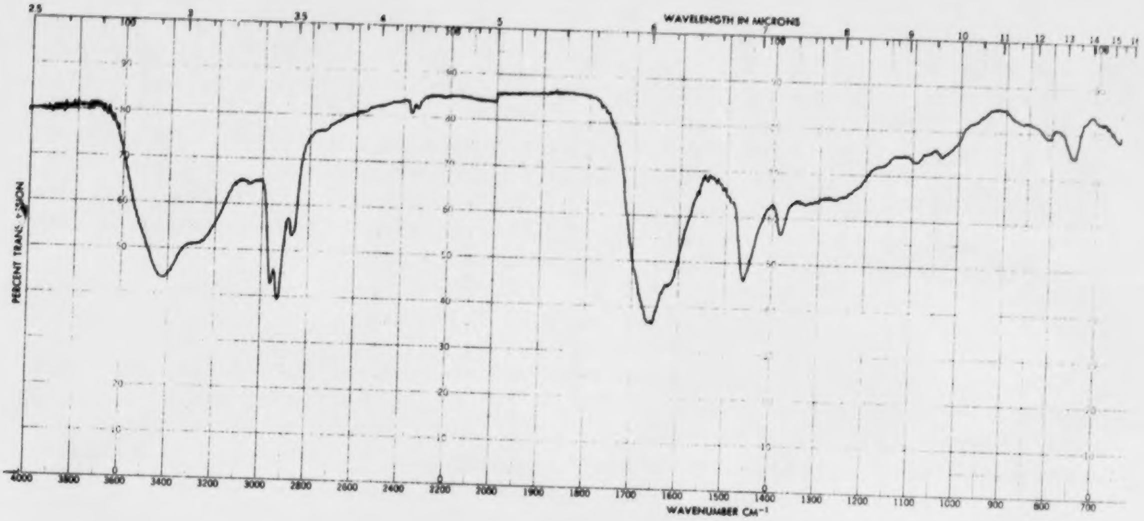

Figure 4. Infrared Spectrum of Methanol Subfraction of Shale Oil.

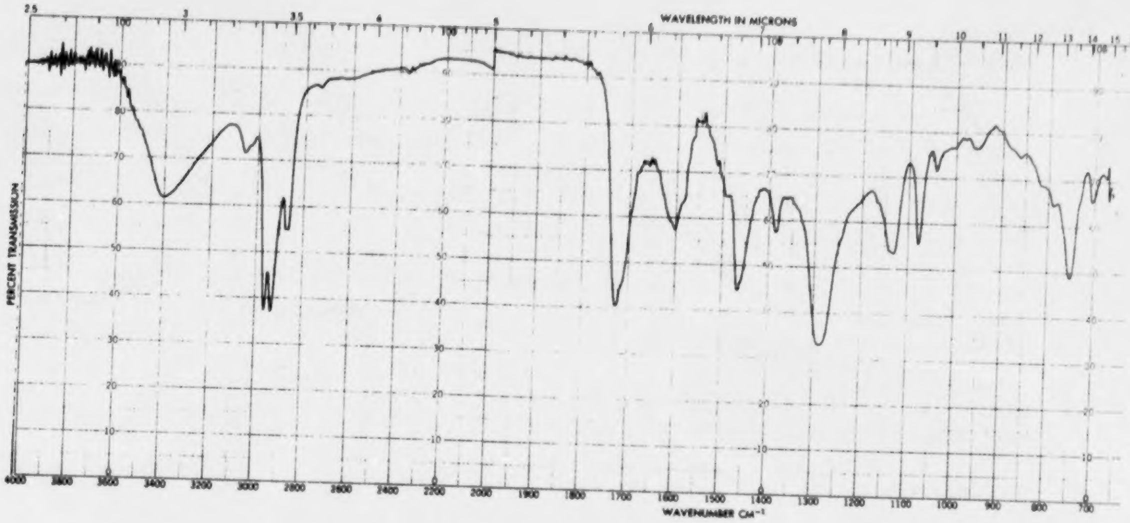

Figure 5. Infrared Spectrum of Methanol Subfraction of Coal Oil C.

nitrogen, and in the latter range by a variety of vinylic protons. In samples such as these, it is difficult to assign functional groupings.

The infrared spectrum of the shale oil subfraction is shown in Figure 4, and that of a coal product in Figure 5. As with the NMR data, because of the complexity of the samples, it is impossible to make specific assignments. The aliphatic bands are clearly seen in the 1385, 1455 and 2800 to 3000 wavenumber regions. The shale oil sample has virtually no aromatic absorption while the coal product does, shown at 1600 and 3000 cm^{-1}. The shale oil has a much stronger carbonyl absorption band than does the coal product (1600 to 1700 cm^{-1}), while both show possible amide or amine absorption (3400 cm^{-1}). There is very little absorption by the shale oil sample in the "fingerprint" region, 750 to 1350 cm^{-1}, while the coal oil has a number of absorption bands in that area.

We have attempted to describe similarities and differences in the polar portions of a variety of types of fossil fuel oils including oil from shale, from several coal liquefaction processes and from a mixture of natural petroleum crudes. Samples have been fractionated by acid/base distribution as well as by gel partition chromatography which was then followed by acid/base distribution and adsorption chromatography. One subfraction of particular interest was that obtained from the hydrophilic fraction after gel partition chromatography, extracted into a neutral subfraction, and then eluted from an alumina column by methanol. This subfraction was not gas chromatographable, and was partially characterized by elemental analysis, NMR spectroscopy and infrared spectrophotometry.

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PROTON AND CARBON-13 NMR STUDIES ON NAPHTHA AND LIGHT DISTILLATE HYDROCARBON FRACTIONS OBTAINED FROM IN SITU SHALE OIL

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ABSTRACT

The proton and carbon-13 NMR studies were made on the saturates, olefins, and aromatic fractions obtained from the naphtha and light distillate cuts of *in situ* shale oil. Carbon-13 NMR area measurements were used to compute the $\overline{C_n/C_1}$ ratio and, thus, the average paraffinic chain length for the saturate fractions. Identification and the relative concentrations of the various olefins were determined from carbon-13 NMR data. The NMR results are compared with the mass spectroanalysis data on the same fractions. The percent of carbon types in the aromatic fractions were also determined by both NMR and mass spectral data. Qualitative agreement between the two techniques was evident. However, some definite disagreement also exists.

INTRODUCTION

Numerous research and technological programs are being conducted by both governmental and industrial laboratories to economically recover oil from the large deposits of oil shale in the Western States of Colorado, Utah, and Wyoming. To aid in monitoring and assessing the various recovery processes being used it is necessary that new analytical methods be developed which are rapid and can qualitatively and quantitatively characterize the various oil fractions obtained from crude shale oil. These fractions are extremely complex mixtures and while, in principle, individual identification of the components is conceptually possible the task would be exceedingly time consuming and of limited value. Characterization in terms of average properties of the sample is an alternate approach. This analytical approach can provide significant quantitative data on the oil samples in a relatively short time. Of the many analytical spectroscopic techniques, NMR spectroscopy is most suitable for obtaining average properties of hydrocarbon fractions.

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Although it is not as sensitive as other instrumental methods, the advantages of NMR spectroscopy are the nondestructive aspects as related to the sample and the relative ease in which the spectroscopic data can be reduced to give the desired information.

Carbon-13 and proton NMR spectroscopy have been used extensively in characterizing oil fractions obtained from petroleum crudes.[1-5] At present, little work using this technique has been published on the chemical composition of shale oil. NMR spectroscopy has been used, however, to study oil shale in the solid state.[7 8 9]

It is the purpose of this paper to present preliminary NMR data on the average composition of the hydrocarbons of the naphtha and light distillate fractions obtained from thermal fractionation of crude shale oil. Both the naphtha and light distillate fractions were subdivided into saturates, olefins, and aromatics. The average carbon chain-length was determined for the saturate fractions. The double-bond position and the relative percent of the various olefin types were determined for the olefin fractions. The aromatic fractions were characterized in terms of average molecular parameters which have been developed for petroleum crude and coal liquid analysis. The data obtained on the saturates, olefins and aromatic fractions by NMR are compared with the mass spectral analysis of the same samples.

EXPERIMENTAL

Shale Oil Fractions

The oil fractions used in this study were obtained from crude shale oil produced by the in situ retort experiment at Site 4, Rock Springs, Wyoming. The crude shale oil was thermally fractionated using the Hempel technique into naphtha, light distillate, heavy distillate, and residue fractions. The naphtha and light distillate fractions were treated with 10% NaOH and 10% H_2SO_4 solutions to remove most of the tar acids and bases,[11] respectively. The neutral fractions were then separated into saturates, olefins, and aromatics using silica gel chromatography.[12] The eluent was monitored by noting changes in the refractive index due to the different hydrocarbon types.

Carbon and Hydrogen Determination

The weight percents of carbon and hydrogen for the shale oil fractions were determined by the standard combustion technique.

Molecular Weight Determination

The molecular weights were determined by vapor phase osmometry. Benzil in benzene was used as a calibrant for VPO molecular weight determinations.

[+] Reference to specific manufacturer does not imply endorsement by the United States Department of Energy.

Nuclear Magnetic Resonance

Carbon-13 NMR--A varian CFT-20 NMR* spectrometer was used to obtain the gated proton decoupled spectra. A 5 mm probe insert was used along with a pulse width of 12 μsec (14 μsec = 90°) and a pulse delay of 9 sec. The number of pulses used was varied to assure good signal-to-noise ratio. Grated decoupling was used to suppress the nuclear Overhauser effect (NOE) and, thereby, assuring quantitative results of the integration of carbon atoms' presence in the samples. Samples were dissolved in $CDCl_3$ and referenced to internal TMS. Spectra were obtained at an ambient temperature of about 38°C.

Proton NMR--Proton spectra were also obtained on the CFT-20 NMR spectrometer with a 5 mm probe insert. A 90° pulse width of 40 μsec was used. In most cases only a single transient was used to record the proton spectra. $CDCl_3$ was used as the solvent for the samples and TMS the internal reference.

Gas Chromatography/Mass Spectrometry

The mass spectral analysis was performed on an AEI-MS12 mass spectrometer and a HP-5700 chromatograph. Data reduction was performed on a Finnigan INCOS 2300 computer system. The mass spectra were recorded at an accelerating voltage of 8KV, an ionizing voltage of 70V, and a filament current of 100 μA. The source temperature was 210°C.

A SCOT column (50' x 0.02") packed with Dexsil 300 was used in the GC. The oven was programmed from 50 to 250°C at 2°/min. Both the transfer line and injection port temperatures were 250°C. A helium flow rate of approximately 4 cc/min was used.

Computer Programs

The equations for computing average molecular parameters from NMR data were obtained from the article by Cantor.[13] The input data for the computation are the normalized integrated areas from both carbon-13 and proton NMR spectra, weight fraction of carbon and hydrogen from elemental analysis and the average molecular weight from VPO.

The method of Robinson and Cook[14] was used to reduce the mass spectral data into compound types in the naphtha and light distillate aromatic fractions.

RESULTS AND DISCUSSION

A number of investigations have been conducted to determine the actual molecular species of alkanes, olefins, and aromatics in naphtha and light distillate fractions of shale oil.[11, 15-21] These studies used techniques other than NMR spectroscopy to determine the hydrocarbon carbon chain length of the most dominant and lesser abundance components. However, such studies were very time consuming.

Table 1 lists the chemical and physical properties of the shale oil fractions obtained from the Hempel distillation of the crude shale oil. Figures 1 and 2 show both the proton and carbon-13 NMR spectra for the saturates, olefins, and aromatics obtained from the naphtha and light distillate fractions, respectively. It is from these spectra that information about the average paraffinic carbon chain-length, olefinic double bond position and average aromatic molecular parameters can be obtained.

Saturates

The proton spectra of the paraffinic carbons of the naphtha and light distillate fractions (Figures 1 and 2, respectively) show little detailed information other than that the ratio of CH_2/CH_3 is greater for the light distillate than the naphtha fraction. Under the experimental conditions used, no evidence for aromatic or olefinic hydrogens can be found indicating that the silica gel separation method is quite satisfactory for saturates.

The carbon-13 spectra for these two fractions shows more detail of the types of carbons present. Again no evidence for aromatic or olefinic compounds can be found. The aliphatic region shows that the saturates are composed essentially of normal alkanes (5 intense resonances) with smaller amount of branched and/or cyclic alkanes. The intensity ratio (as well as the area ratio) for the five most intense lines differ for the naphtha and light distillate fraction. This difference is due to the average carbon chain-length of the n-alkanes present in each fraction. The average carbon chain-length in the saturates can be estimated from NMR area ratios of known n-alkanes. For example, Figure 3 shows the carbon-13 spectra of two n-alkanes-nonane and hexadecane. The methyl carbon resonance is at 14.2 ppm relative to TMS. Carbons 2, 3, 4, and 5 resonate at 23.0, 32.3, 29.7, and 30.0 ppm, respectively. The area of the resonance at 14.2 ppm represents two methyl carbons and is sufficiently upfield to be integrated without difficulties even in complex systems. Carbon 4 and higher have similar chemical shifts (∿30.0 ppm) and, thus, must be integrated together to obtain the total area. In complex systems these carbons may not always be resolved.

The area ratio of C_n (n = 4,5,6 . . .) to C_1 was obtained for a series of n-alkanes and this ratio was plotted against the number of carbons in the molecule (see Figure 4). The solid line in Figure 4 represents the theoretical values obtained for the hydrocarbons investigated. Since the experimental values obtained fall on the line or nearly so indicates the spectrometer conditions are such that quantitative results can be obtained for carbon-13 studies.

The area ratios of C_n to C_1 for the saturates of the naphtha and light distillate fraction were found to be 2.07 and 3.67, respectively, corresponding to an average carbon chain-length of C_{10} and $C_{13\ 14}$, respectively. The mass spectral analysis of the saturates obtained from the naphtha and light distillate fraction is given in Table 2.

Table 1. CHEMICAL AND PHYSICAL PROPERTIES OF SHALE OIL FRACTIONS

	Dry shale oil	Naphtha	Light distillate	Heavy distillate	Residue
Boiling range		IBP-400°F	400-600°F	600-800°F	800+°F
Fraction yield, vol %		12.2	39.8	31.7	12.6
Paraffins and cyclo-paraffins, vol %		65.2	60.5		
Olefins and cyclo-olefins, vol %		11.1	11.1		
Aromatics, vol % (includes sulfur, nitrogen and oxygen compounds)		23.7	24.8		
Carbon, wt %	84.96	84.69	85.35	85.13	82.81
Hydrogen, wt %	11.97	12.94	12.42	11.89	10.56
Nitrogen, wt %	1.50	1.04	1.16	1.59	2.20
Sulfur, wt %	0.95	0.69	0.44	0.52	0.94
Oxygen, wt %					
VPO molecular weight (ave.)		199	204	290	
Tar acids, vol %		3.6	1.6		
Tar bases, vol %		6.6	9.9		

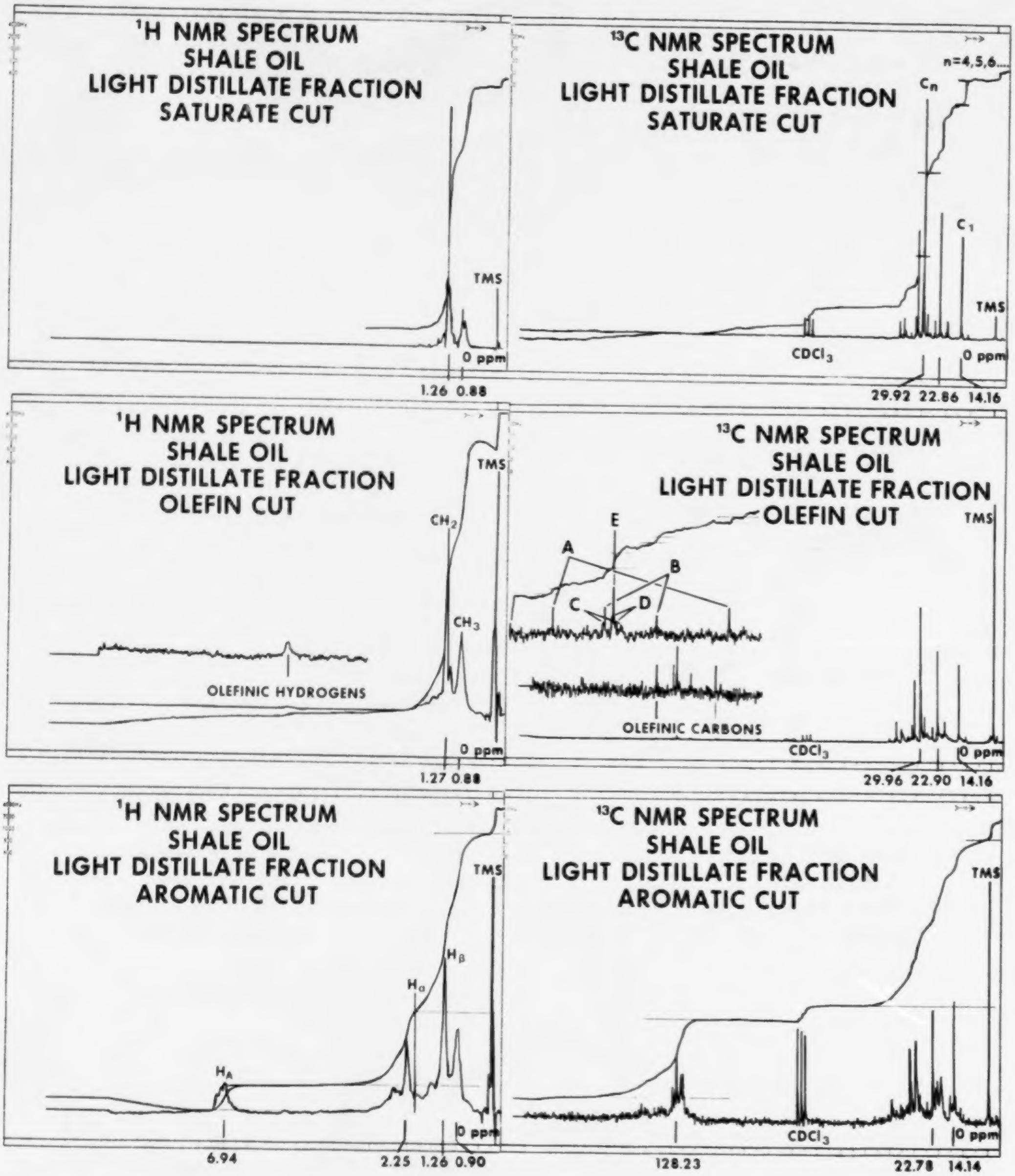


Figure 1. Proton and Carbon-13 NMR Spectra of the Naphtha Saturate, Olefinic, and Aromatic Fractions.

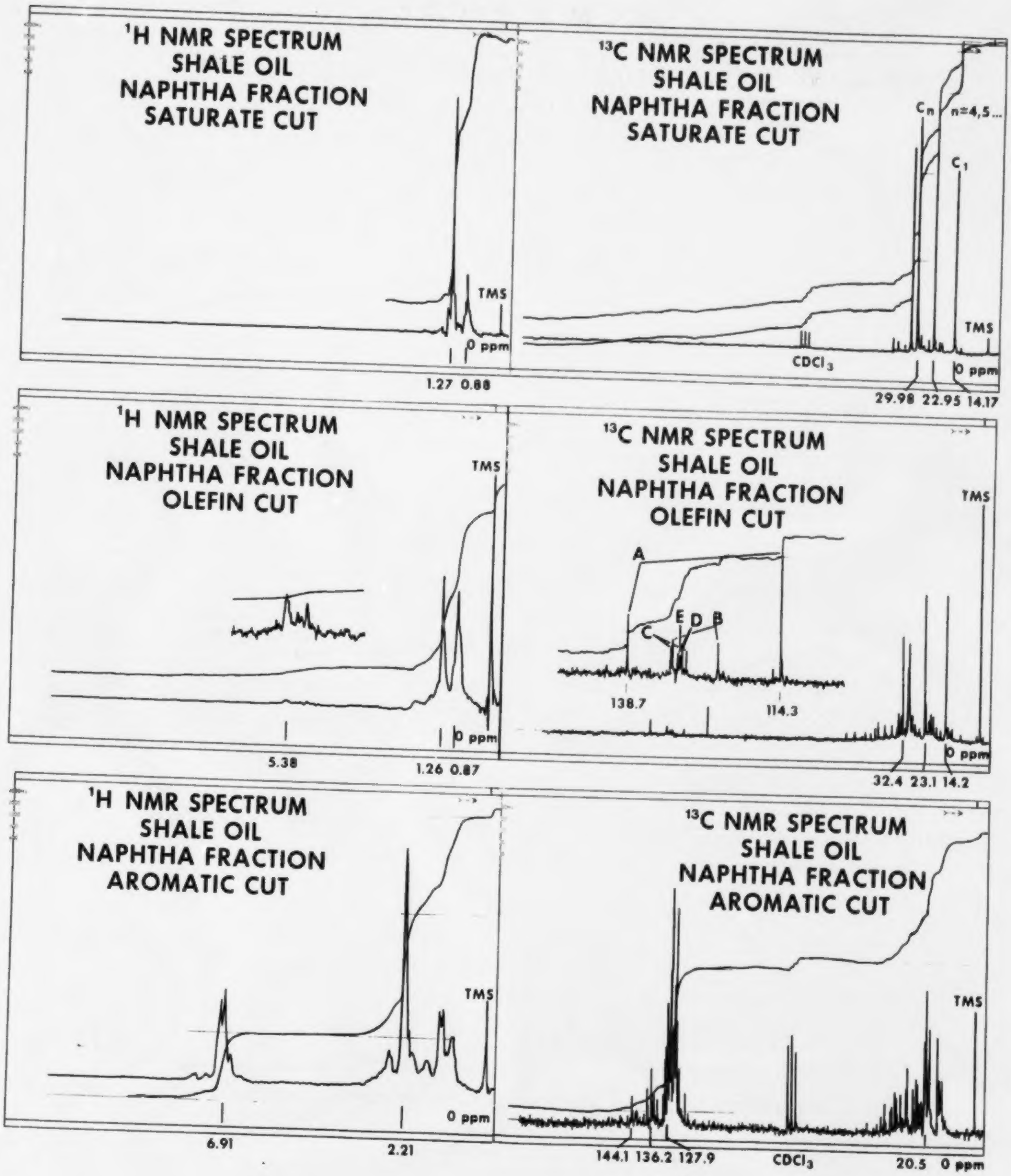


Figure 2. Proton and Carbon-13 NMR Spectra of the Light Distillate Saturate, Olefinic, and Aromatic Fractions.

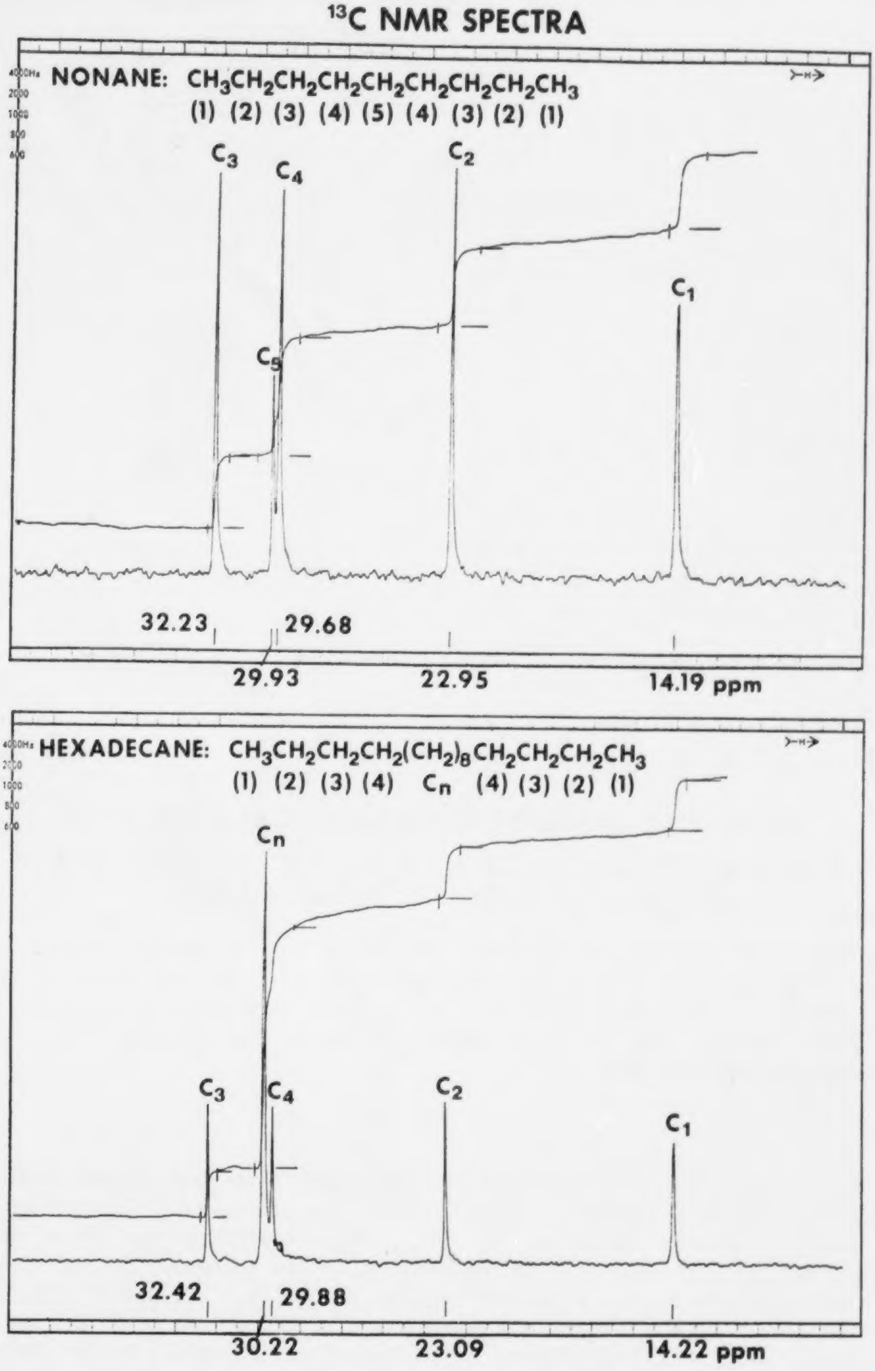


Figure 3. Carbon-13 NMR Spectra of Nonane and Hexadecane.

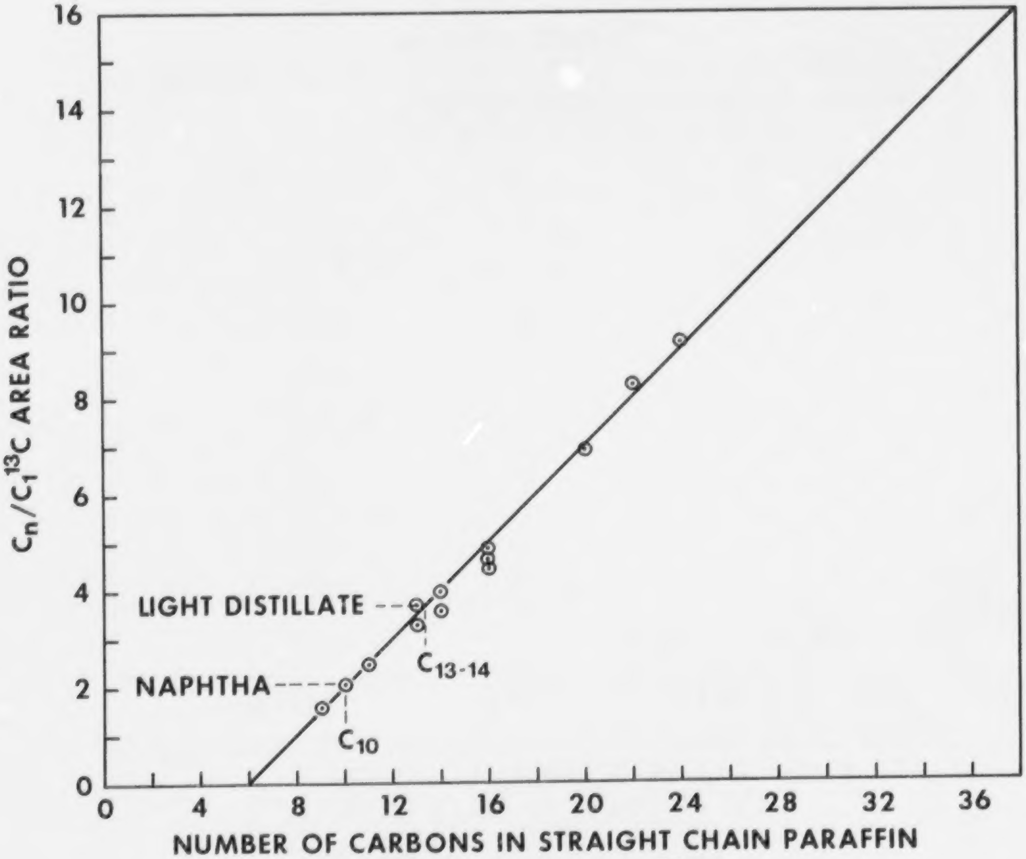


Figure 4. Correlation of the $C_n/C_1\ ^{13}C$ Area Ratio with the Number of Carbons in Normal Alkanes.

From the mass spectral data the saturates are composed essentially of n-alkanes. The dominant n-alkanes for the saturates in the naphtha fraction are n-C_{10} and n-C_{11} and for the light distillate fractions n-C_{12}, n-C_{13}, and n-C_{14}. These values are in good agreement with the average carbon chain-length as determined by NMR.

Olefins

The proton spectra of the olefins obtained from the naphtha and light distillate fractions (Figures 1 and 2) show the presence of olefinic hydrogens at about 5.38 ppm relative to TMS. The aliphatic region shows large amounts of methyl and methylene hydrogens. The carbon-13 spectra shows well-defined olefinic carbons in the region of 114 to 138 ppm. The chemical shifts of the long chain saturate carbons in 1-alkene are similar to carbons in long chain saturate n-alkanes. The saturate carbon region shows fine intense resonances at 14.24, 23.08, 29.63, 29.86, and 32.41 ppm for the naphtha fraction and 14.16, 22.90, 29.64, 29.96, and 32.20 ppm for the light distillate fraction. The observed intense resonances in the alkane region

TABLE 2. MASS SPECTRAL ANALYSIS OF SATURATES

	Naphtha Fraction Area %	Light Distillate Fraction, Area %
Branched C_9	1.8	
n-C_9	1.8	
n-C_{10}	26.5	
Branched C_{11}	4.0	
n-C_{11}	39.7	2.6
n-C_{12}	13.1	14.5
Branched C_{13}	1.4	
n-C_{13}	2.4	16.7
n-C_{14}		11.0
Branched C_{14}		5.4
n-C_{15}		7.9
Branched C_{15}		5.1
n-C_{16}		6.8
Branched C_{16}		6.9
n-C_{17}		8.2
Branched C_{17}		2.7
n-C_{18}		4.6
Total Straight Chain	83.5	72.4
Total Branched	7.2	20.2
Unidentified	9.3	7.4

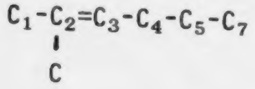
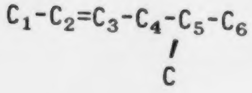
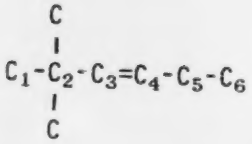
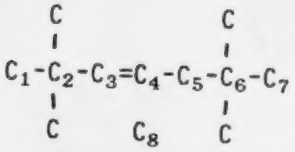
of the olefins in most cases differ only 0.06 ppm from the intense resonances observed in the corresponding saturate fractions. It would be difficult to ascertain whether or not these resonances are associated with olefins or saturates based on chemical shift data only. The intensities observed for the CH_3 carbons do not correspond to the intensities of the olefinic carbons. This suggests that the olefins were incompletely separated from the saturates using the silica gel separation method and confirms the findings of other investigators.[15-21]

Since any contamination of the olefins by saturates will not interfere with the olefinic carbon region, it is possible to identify the most dominant alkene double bond positions and determine their corresponding mole ratios. Table 3 lists the normal alkenes identified in the olefin subfractions isolated from the naphtha and light distillate fractions. Also included in the table are the observed chemical shifts of the alkene carbons and the relative percent for each of the alkenes identified. The alkene double bond positions were identified by comparing the observed chemical shifts with those reported by Couperus et al.[22] Of the 70 compounds investigated by Couperus et al., only four of the branched olefins listed

Table 3. ^{13}NMR CHEMICAL SHIFTS AND MOLE RATIOS OF NORMAL OLEFINS IN NAPHTHA AND LIGHT DISTILLATE FRACTIONS OBTAINED FROM SHALE OIL

Designation in spectra (Figs. 1 & 2)	Double bond position n-ene	Naphtha fraction			Light distillate fraction		
		Chemical shift (ppm)		Relative percent	Chemical shift (ppm)		Relative percent
		C_n	C_{n+1}		C_n	C_{n+1}	
A	1-ene	114.34	138.67	36	114.21	138.95	21
B	2-ene	124.44	131.68	11	124.46	131.73	18
C	3-ene	131.92	129.44	11	131.91	129.42	--
D	4-ene	130.16	130.69	42	130.12	130.66	61
E	5-ene	130.40	130.40		130.41	130.41	

TABLE 4. POSSIBLE BRANCHED OLEFINS FROM NMR DATA

	Alkene Carbons, Chemical Shifts (ppm) C_n	Alkene Carbons, Chemical Shifts (ppm) C_{n+1}
 $C_1-\underset{\overset{|}{C}}{C_2}=C_3-C_4-C_5-C_7$	131.29[a] (131.68)[b]	124.96 (124.44)
 $C_1-C_2=C_3-\underset{\overset{/}{C}}{C_4}-C_5-C_6$	124.41 (124.44)	129.67 (129.49)
 $C_1-\overset{\underset{|}{C}}{\underset{\overset{|}{C}}{C_2}}-C_3=C_4-C_5-C_6$	139.21 (138.67)	130.73 (130.69)
 $C_1-\overset{\underset{|}{C}}{\underset{\overset{|}{C}}{C_2}}-C_3=\underset{C_8}{C_4}-C_5-\overset{\underset{|}{C}}{\underset{\overset{|}{C}}{C_6}}-C_7$	138.86 (138.67)	131.79 (131.68)

[a] Chemical shift values from Reference 22.
[b] Observed chemical shift values.

have chemical shifts which correspond to the observed shifts measured within ±0.6 ppm. These branched olefins are shown in Table 4. It is the position of the double bond relative to the methyl substitution that is important since the actual hydrocarbon chain may be longer for the olefins in the samples. A longer hydrocarbon chain would have little effect on the olefinic carbons' chemical shifts. The data in Table 3 indicates that the light distillate fraction contains more symmetrical alkenes relative to 1-alkene than found in the naphtha fraction.

The mass spectral analysis (in area percent of the olefins obtained from the naphtha fraction indicates that the most predominant alkenes are the n-C_{11} (24.8%) and branched C_{11} (17.1%). The total amount of normal olefins was found to be 36.4% and branched olefins 29.6%. The remaining fraction was due to normal alkanes as suspected from NMR data. The distribution of the chain-length of the alkenes were found to be almost identical to the alkanes in the saturate fraction.

The predominant alkenes found in the olefins obtained from the light distillate fraction were C_{12} C_{13}, and C_{14}. The mass spectral analysis also showed large amounts of alkanes of similar chain-length.

Aromatics

The proton and carbon-13 NMR spectra of the aromatic components in naphtha and light distillate fractions are shown in Figures 1 and 2, respectively. The proton spectra of the aromatic naphtha and aromatic light distillates shows considerable detail in the types of protons present. In the naphtha fraction, there is evidence of proton resonance for small amount of di-and triaromatic molecules. There appears to be no evidence of this kind in the light distillate fraction at the recorded signal-to-noise level. The relative amount of aromatic protons is also less in the light distillate than in the naphtha fraction (8.7% and 23.8%, respectively). Another significant difference between the fractions is the ratio of CH_3 and CH_2 hydrogens relative to the α-CH_2 hydrogens. The naphtha fraction has more α-CH_2 (42%) than the light distillate fraction (26.6%). Thus, the proton NMR data suggest the naphtha fraction contains mostly substituted monoaromatic compounds with apparently small amount of di- and triaromatic molecules. The light distillate fraction is composed mostly of monoaromatics which are less substituted, but the alkane substituent is of longer chain-length.

The carbon-13 spectra of the aromatics for both the naphtha and light distillate fraction (54% and 32%, respectively). The relative amounts of alkane carbons were found to be 46% and 68% for the naphtha and light distillate fractions, respectively.

Average molecular parameters were calculated for both the naphtha and light distillate fractions using the equations listed in the paper by Cantor.[13] The mass spectral data were also obtained for the aromatic cuts of the naphtha and light distillate fractions. The Robinson-Cook method[14] of treating mass spectral data of complex aromatic mixtures was used to obtain information on the type and amount of aromatic molecules present.

The mass spectral data show that the aromatic fractions are free of any cross-contamination due to saturate hydrocarbons. There is considerable agreement between the NMR and mass spectral data. However, some definite disagreement also exists and these differences are being studied in detail.

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A CONTINUOUS FLOW BIOASSAY TECHNIQUE FOR ASSESSING THE TOXICITY OF OIL SHALE RELATED EFFLUENTS: PRELIMINARY RESULTS WITH TWO SPECIES OF CADDISFLY LARVAE

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INTRODUCTION

The following report describes research results of a study to develop preliminary methods for determining the response of selected species of aquatic insects to an effluent associated with activities of the oil shale industry.

The wastewater considered is a byproduct of in situ retorting of oil shale deposits and includes water of hydration, combustion water and intruding groundwater. These waters typically contain organic compounds in concentrations of up to 2% and inorganics to 5%, depending on the processing parameters and the extent of groundwater intrusion. The principal inorganic components of the wastewater are ammonium, sodium and bicarbonate with lesser but significant amounts of thiosulfate, chloride, sulfate and carbonate.

Large scale commercial shale oil production has yet to take place. However, the effect on aquatic insects of wastewaters from conventional petroleum production may give an indication of the responses that would result from oil shale processing effluents. The impact of crude oil on natural communities of benthic macroinvertebrates has been studied by Rosenberg and Weins[1] and Vascotto,[2] of heavy bunker oil by McCauley,[3] and of oil field brines by Mathis and Dorris.[4] Larval insect populations occurring in oil refinery effluent holding ponds were reported by Tubb and Dorris.[5] Although the responses were markedly species specific, in general Diptera were the most tolerant of petroleum pollution while Trichoptera, Ephemeroptera and Plecoptera were the most sensitive.

The potential for use of stream macroinvertebrates as water quality indicators stems from their relative ease of collection, wide range of tolerance to pollution, inability to leave a polluted area rapidly, and often ready adaptability to laboratory study.[6] The caddiflies (Insecta: Trichoptera) in particular are frequently used as indicator organisms for freshwater lotic habitats because of their nearly ubiquitous occurrence, their frequent dominance in both diversity and abundance, and the narrow pollution tolerances of many species.[7 8]

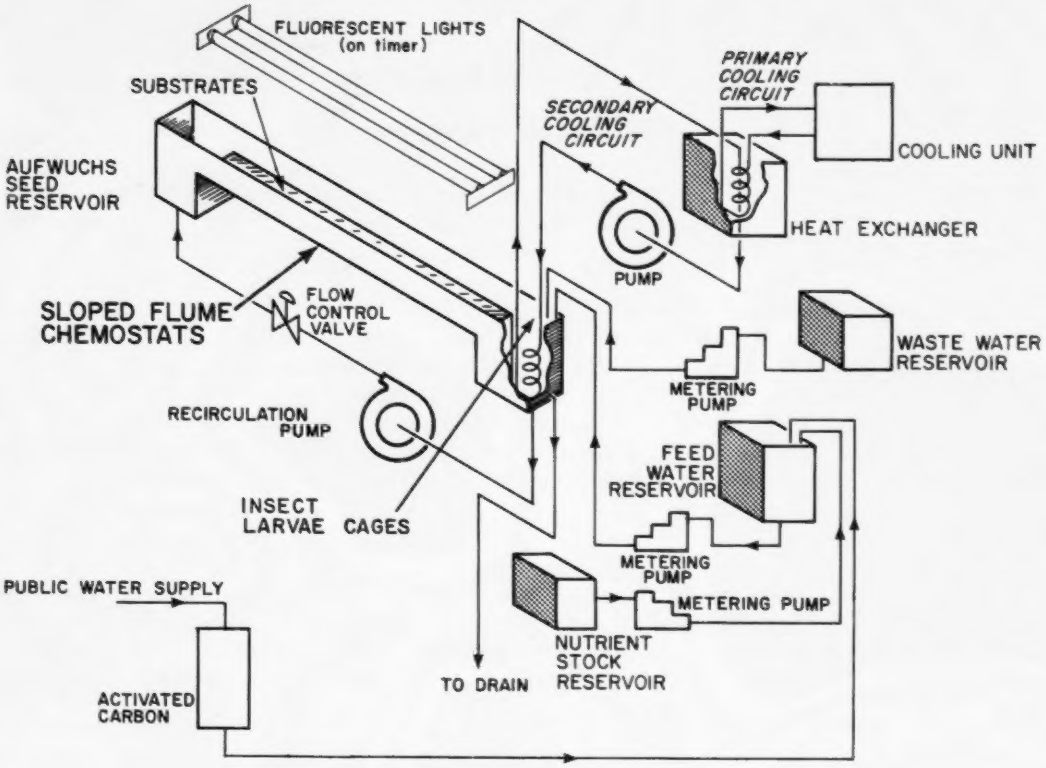
Apparati to simulate the lotic milieu of caddisfly larvae have been designed and successfully employed without resorting to elaborate or expensive support systems.[9-13] Many utilize flumes with or without water recirculation but simpler designs involving small, agitated basins are also effective. The most important considerations pertaining are water circulation, maintenance of a high dissolved oxygen concentration, and prevention of temperature extremes.

Two experimental runs were performed in which caddisfly larvae were exposed to various dilutions of oil shale related wastewaters in a model stream setting. Another run used a synthetic wastewater compounded from ammonium carbonate. In addition, one run tested the effect of the experimental apparatus, with no wastewater load, on the caddisfly larvae. The activity of the larvae was observed in terms of its motility, prepupation behavior and timing, and the abandonment of larval cases.

METHODS

Two species were used in the bioassays, Dicosmoecus gilvipes (Hagen) (Trichoptera: Limnephilidae) and Gumaga nigricula (McLaughlin) (Trichoptera: Sericostomatidae). The test organisms were collected from Big Sulfur Creek at The Geysers, Sonoma County, California. Last instar Gumaga and late instar Dicosmoecus were used.

The laboratory bioassays were conducted in four mutually isolated, parallel model streams. Figure 1 shows a schematic of the bioassay apparatus and support system with one stream illustrated. Each stream consisted of a riffle reach 120 cm long bounded by a pool at each end. The upstream and downstream pools were 17-cm and 27.5-cm long, respectively. The width of the riffles and pools was 9.5 cm, yielding a total volume of 12 liters per stream. Flow was produced in the streams by pumping water from the lower pools to the respective upper pools. Temperature control was effected by means of a cooling coil in the lower pool of each stream. An array of fluorescent tubes suspended over the riffles provided illumination. Although well lit, no lights were situated directly over the pools. Chemical constancy of the stream waters was maintained by metering makeup water to the streams on a continuous basis. The makeup water source was Berkeley (East Bay Municipal Utilities District) tap water, dechlorinated by passage through a column of activated carbon. Since concurrent aufwuchs bioassays were being conducted in the riffle reaches of the model streams, nutrient salts were added to the makeup water to promote primary productivity. The millimolar (mM) concentrations of the salts in the tap water and of the salts added are given on Table 1. The resulting concentrations are similar to those suggested by Guillard with reduced nitrate content and neither vitamin nor buffer addition.[14] In addition, the wastewater load indicated



XBL 779-1907

Figure 1. Model Stream Schematic.

TABLE 1. IONIC COMPOSITION OF MODEL STREAM MAKEUP WATER
All Values in mM, T=Trace

Constituents	Millimolar Concentration In Tap	 Added	 Total
Ca^{++}	0.45	0.0	0.45
Mg^{++} (as $MgSO_4 \cdot 7H_2O$)[a]	0.123	0.027	0.150
HCO_3^-	0.865	0.0	0.865
$PO_4^{\equiv}$ (as H_3PO_4)[a]	0.0002	0.0485	0.0487
NO_3 (as $NaNO_3$)[a]	0.0015	0.0986	0.1001
SiO_2	0.120	0.0	0.120
K^+ (as KCl)[a]	0.015	0.064	0.079
EDTA (as Na_2EDTA)[a]	-[d]	0.01	0.01
FE^{+++} (as $FeCl_3 \cdot gH_2O$)[a]	0.002	0.010	0.012
Cu^{++} (as $CuSO_4 \cdot 7H_2O$)[a]	-[d]	<0.01	T
Zn^{++} (as $ZnSO_4 \cdot 7H_2O$)[a]	<0.01	<0.01	T
Co^{++} (as $CoCl_2 \cdot 6H_2O$)[a]	<0.0001	<0.0001	T
Mn^{++} (as $MnCl_2 \cdot 4H_2O$)[a]	0.0003	0.0006	0.0009
Mo^{+++} (as $Na_2MoO_4 \cdot 2H_2O$)[a]	<0.01	<0.01	T
Na^+ [c]	0.3045	0.1246	0.4291
Cl^- [c]	0.169	0.096	0.265
$SO_4^=$ [c]	0.16	0.03	0.19

[a] Compound was used to supply the ion.

[b] Typical values for East Bay Municipal Utilities District, average of analyses for December 1976.

[c] Source from several compounds listed above.

[d] Not reported.

for each stream by the design of each experimental run was fed with the makeup water. The metered makeup water displaced an equal volume of stream water to waste which left the system via overflow ports in stilling wells connected to each stream. The rate of makeup water feed was adjusted to deliver six stream volumes per day for a mean residence time of 4 hours.

Ammonia levels in the model stream water were measured by the phenol-hypochlorite method.[15] Aside from hydrogen sulfide, which was probably absent from the well aerated stream waters, this colorimetric technique is quite insensitive to interfering substances as well as other nitrogenous compounds. Interference from color-producing compounds in the wastewater was probably negligible because of the high dilutions employed.

The test larvae were confined in cages of PVC screen located in the lower pool of each stream. A minimum of 16 cm^3 (1 $in.^3$) was provided for each individual. In addition to PVC, other materials in contact with the stream water were Teflon, nylon, white epoxy paint, polyethylene, plexiglass and steel.

The effluent dilutions in each stream for the four experimental runs are presented on Table 2 along with the mean temperature, pH, and ammonia concentrations. For each run, a one-way analysis of variance was performed on the temperature and pH values summarized on Table 2. Stream number was used as the independent variable in the analyses. The variations in temperature were not significantly influenced by stream number in any of the runs. The measured pH values, however, did vary significantly ($p < 0.015$) with stream number in each run except Run 2, when it was not significantly different between streams. The stream dependence of the measured pH values is primarily a reflection of the salts in the effluents and of the impact of the primary productivity in each of the streams on the carbonate buffer system. The streams' pH values for each run were compared using Scheffe's test, at the 0.05 level of significance, as implemented by the system of computer programs from the _Statistical Package for the Social Sciences_.[16] The streams in each run whose pH values were not different from each other at this level of significance are joined by the vertical bars on Table 2.

Run 1, 1/7/78 to 1/19/78, was a demonstration of the viability of _Gumaga nigricula_ larvae in the model streams with no wastewater addition. The duration of Run 1 was 12 days. Each of the other three runs lasted 9 days. The test specimens were collected on 1/4/78 and within 6 hours were transported to the laboratory where they were introduced to an aerated basin of model stream water. The stock basin was maintained near the temperature of the model streams. Larval mortality in the stock basin prior to the beginning of each run was negligible. The test larvae were randomly distributed to the cages in the lower pool of each stream.

The wastewater examined in Run 2 was a water sample obtained from the U.S. Department of Energy/Laramie Energy Technology Center as produced during the Rock Springs Site 9 experimental _in situ_ oil shale processing project near Rock Springs, Wyoming.[17] This effluent, called Omega-9 water, was filtered to effect a nominal 0.4 μm exclusion of suspended matter prior

Table 2: PHYSICAL/CHEMICAL MEASUREMENTS ON THE MODEL STREAMS FOR THE FOUR EXPERIMENTAL RUNS. TEMPERATURES AND pH VALUES ARE MEANS OF DAILY IN SITU MEASUREMENTS TAKEN IN RIFFLE REACHES. THE VERTICAL BARS TO THE RIGHT OF THE pH COLUMN CONNECT STREAMS WHOSE pH VALUES ARE NOT SIGNIFICANTLY DIFFERENT AT THE 0.05 LEVEL AS MEASURED BY SCHEFFÉ'S TEST. MEASURED AMMONIA VALUES ARE MEANS OF TRIPLICATE SAMPLES TAKEN ON THE LAST DAY OF EACH RUN. NO AMMONIA MEASUREMENTS WERE TAKEN FOR RUN 1.

Run No.	Effluent	Dilution	Stream No.	Temperature (C) Mean (Range)	pH Mean (Range)	Ammonia (mM) Calc.	Ammonia (mM) Meas.
1	NONE	0	1	24.3 (23.7 - 25.1)	8.8 (8.6 - 9.0)	0	-
		0	2	24.4 (23.9 - 25.3)	9.1 (8.9 - 9.4)	0	-
		0	3	24.6 (24.0 - 25.3)	9.0 (8.7 - 9.3)	0	-
		0	4	24.5 (24.0 - 25.3)	9.1 (8.9 - 9.3)	0	-
2	FILTERED OMEGA-9 WATER	0	4	21.7 (20.8 - 22.9)	7.9 (7.0 - 8.5)	0	0
		0.27%	3	21.8 (20.8 - 23.3)	8.1 (7.6 - 8.4)	0.59	0.44
		1.06%	2	22.0 (21.0 - 23.3)	8.2 (7.7 - 8.5)	2.36	2.02
		2.12%	1	21.7 (20.7 - 23.0)	8.3 (7.8 - 8.4)	4.73	4.22
3	UNFILTERED OMEGA-9 WATER	0	1	24.0 (22.9 - 24.9)	8.6 (7.7 - 8.9)	0	0
		0.27%	3	24.4 (23.4 - 25.1)	7.6 (6.7 - 8.2)	0.59	0.08
		0.53%	2	24.4 (23.2 - 25.1)	7.6 (7.0 - 8.1)	1.18	0.47
		1.06%	4	24.5 (23.4 - 25.2)	8.2 (8.0 - 8.3)	2.36	2.37
4	AMMONIUM CARBONATE	0	3	23.3 (22.3 - 24.2)	8.5 (7.5 - 9.1)	0	0
		0.56 mM NH_3	4	23.7 (22.7 - 24.6)	7.1 (6.9 - 7.3)	0.56	0.04
		2.26 mM NH_3	1	23.2 (22.1 - 24.1)	6.9 (6.0 - 8.1)	2.26	0.51
		4.52 mM NH_3	2	23.4 (22.4 - 24.3)	7.2 (6.4 - 8.4)	4.52	1.25

TABLE 3. WATER QUALITY CHARACTERIZATION OF OMEGA-9 WATER[a]

Alkalinity (as $CaCO_3$)	16,200.0 ±480.0
Biochemical Oxygen Demand, 5-day	740.0
Carbon, Bicarbonate (as HCO_3^-)	15,940.0
Carbon, Carbonate (as $CO_3^{=}$)	500.0
Carbon, Inorganic (as C)	3340.0 ± 390.0
Carbon, Organic (as C)	1003.0 ± 192.0
Chemical Oxygen Demand	8100.0 ± 5700.0
Conductivity (μmho/cm)	20,400.0 ± 3840.0
Cyanide (as CN^-)	0.42 ± 2.9
Hardness, Total (as $CaCO_3$)	110.0
Nitrogen, Ammonia[b] (as NH_3)	3795.0 ± 390.0
Nitrogen, Ammonium (as NH_4^+)	3470.0 ± 830.0
Nitrogen, Kjeldahl (as N)	3420.0 ± 420.0
Nitrogen, Nitrate (as NO_3)	0.17
Nitrogen, Oranic (as N)	148.0 - 630.0
Oil and Grease	580.0
pH	8.65 ± 0.26
Phenols	60.0 ± 30.0
Phosphorus, Orthophosphate (as $PO_4^{\equiv}$)	0.08 - 24.6
Solids, Fixed (550 C)	13430.0 ± 415.0
Solids, Total (103-105 C)	14210.0 ± 120.0
Solids, Total Dissolved	14210.0 ± 193.0
Sulfur, Sulfate (as $SO_4^{=}$)	1990.0 ± 250.0
Sulfur, Sulfide (as S)	0.0
Sulfur, Sulfite (as S)	<20.0
Sulfur, Tetrathionate (as $S_4O_6^{=}$)	280.0
Sulfur, Thiosulfate (as $S_2O_3^{=}$)	2740.0 ± 730.0
Sulfur, Thiocyanate (as SCN^-)	123.0 ± 18.0

[a] All values are mg/l unless otherwise noted.[18]
[b] This is the sum of NH_3 and NH_4^+.

to its distribution to research laboratories. A description of the filtered Omega-9 water in terms of its water quality parameters is given on Table 3. Although the Omega-9 water sample was probably the best in situ retort water currently available, it is not necessarily representative of waters which may be produced during full scale commercial in situ oil shale processing. Consequently the results are strictly applicable to this water only. the stream water effluent concentrations tested in Run 2 were 2.12%, 1.06% and 0.27% as well as a control stream with no Omega-9 water loading. In Run 2, 2/13/78 to 2/22/78, Gumaga nigricula larvae collected from Big Sulfur Creek on 2/12/78 were used. Transportation to the laboratory was the same as with the 1/4/78 collection. Unlike the earlier run, allochthonous leaf matter from the collection site was included in the larvae cages of each stream.

On 3/13/78 Gumaga nigricula larvae for Run 3, 3/15/78 to 3/24/78, were collected and transported to the laboratory as in the previous runs. Allochthonous stream leaf matter was collected for introduction to the insect cages in the model streams. Unfiltered Omega-9 water was used for Run 3. The concentrations used were 1.06%, 0.53%, 0.27% and 0%.

Run 4 was designed to determine the effect of ammonium carbonate, potentially a biolobically critical component of untreated oil shale related effluents, on two species of caddisfly larvae. Gumaga nigricula and Dicosmoecus gilvipes larve were collected on 4/21/78 from Big Sulfur Creek along with a supply of allochthonous leaf matter for the run, 4/22/78 to 5/1/78. The ammonium carbonate concentrations tested were 4.52 mM, 2.26 mM, 0.56 mM plus a control receiving no salt.

A period of at least one week was allowed to elapse between runs during which the streams were flushed with makeup water containing no wastewater. After each run the riffles and PVC insect cages of each stream were scrubbed to remove any aufwuchs accumulation. The stream chosen as the control was changed for each run.

RESULTS

Table 4 details the response of the caddisfly larvae for each of the three runs in which wastewater was applied. The disposition of the initial number of larvae in each stream is partitioned between the categories "active," "prepupae," "pupae," "dead or moribund" and "missing." To warrant "active" status a larva must extend its legs beyond the case and crawl around. This criterion was usually easily observed as the species studied were quite motile in the stream cages. In some instances larvae had turned around in their cases or begun pupating by sealing one end of their cases and/or attaching their cases to the cage or the allochthonous leaf matter with silk threads. These larvae were designated "active" as long as extended moving legs were visible. All larvae not active for longer than a day were removed from the stream and preserved. At the end of each of the last three runs all larvae were preserved for postmortem examination when the inactive individuals were determined to be "prepupae" (in the sense of Wiggins),[19] "pupae" or "dead or moribund." Also designated "dead or moribund" were larvae which abandoned their cases whether still motile or not.

TABLE 4. INSECT LARVAE BIOASSAY RESULTS

		Initial No.	Active	Prepupae	Pupae	Dead or moribund	Missing
RUN 2							
Gumaga nigricula	0.0%	17	16	0	1	0	0
	0.27%	15	15	0	0	0	0
Filtered Omega-9	1.06%	15	14	1	0	0	0
Water	2.12%	16	14	2	0	0	0
RUN 3							
Gumaga nigricula	0.0%	18	13	2	2	1	0
	0.27%	14	9	2	3	0	0
Unfiltered	0.53%	18	12	3	2	1	0
Omega-9 Water	1.06%	18	13	2	0	3	0
RUN 4							
Gumaga nigricula	0.0mM	9	5	2	1	0	1
	0.56mM	11	8	3	0	0	0
Ammonium	2.26mM	10	5	3	1	1	0
Carbonate	4.52mM	9	4	3	1	1	0
RUN 4							
Dicosmoecus gilvipes	0.0mM	10	9	0	0	0	1
	0.56mM	9	8	0	0	1	0
Ammonium	2.26mM	9	2	0	0	1	4
Carbonate	4.52mM	10	4	0	0	4	2

The decision to classify these larvae as dead stems from the assumption that the decased condition would be fatal within a short period of time. "Missing" larvae were noted in Run 4 only.

The results of Run 1 are not shown on Table 4 because only one inactive specimen occurred over the course of the 12 days. Of the ten Gumaga nigricula larvae in each stream at the beginning of this run, one larva from stream number 1 sealed the ends of its case and attached itself to the PVC screen cage as though entering pupation. The specimen was unfortuantely not preserved to later determine if the pupation process had begun. This larva became inactive on the fourth day of the run. On the seventh day of Run 1, one larva in stream number 2 became inactive and sealed the ends of its case but by the next day it had unsealed the case and begun crawling around again. It remained active through the end of the run.

DISCUSSION

The survival and activity data for two species of caddisflies determined from Runs 1-4 provide an example of the potential information that can be obtained from bioassay analysis to assess the environmental effects of oil shale related effluents. As discussed below, these results are intended as a demonstration of this bioassay technique. Undoubtedly, if this approach is expanded or modified to answer specific biological questions regarding the effects of particular effluents, a useful and additional dimension to water monitoring programs associated with the development of the oil shale industry will be provided.

Run 1 demonstrates that Gumaga nigricula larvae remain "active" under model stream conditions for at least 12 days. Since the duration of the subsequent runs was only nine days each, it is expected that the larvae could adequately accommodate any stream-induced stress for that period of time. The survival of Gumaga nigricula as larvae in the control streams in the following three runs was usually not as high as with Run 1. Most Gumaga nigricula larvae remained "active" in the Run 2 control stream (94%); however, in Runs 3 and 4 only 72% and 56%, respectively, were "active: in the control streams for nine days.

Perhaps the elevated temperature of the streams precipitated pupation in the Gumaga nigricula which were obtained from a much cooler environment, 10°C to 12°C. Since specimen collection was never more than three days from the beginning of each of the runs, stress from residence in the stock basin was not likely to be responsible for the inactivity. Probably the condition of the larvae in Big Sulfur Creek at the time of collection was the most important factor influencing the number of inactive specimens in the control streams. Although the streams were allowed time to flush out any effluent residual from the previous run before commencing a new run, the possibility exists that some toxic components may have adsorbed to the stream surfaces and been slowly released to the stream waters of the subsequent run. No analyses were performed to assess the significance of this mechanism. It is likely that any chemical carryover was minor because all unscrubbed stream surfaces were covered with a dense mat of aufwuchs that was continually sloughing cells, which were carried to waste via the overflow, and regenerating itself with new cell growth. Thus any toxins concentrating in the aufwuchs would presumably be depleted during the interrun periods. Given the heavy aufwuchs growth, probably negligible amounts of effluent constituents were adsorbed to the underlying model stream surfaces. It should be noted that the phenomenon of fewer control stream larvae remaining "active" with each successive run could be attributed either to progressive maturity of the last instar larvae collected from Big Sulfur Creek for each run, or to residual toxicity buildup in the streams. Neither hypothesis can be disproven by the data, but distinct differences in larval responses between the proven by the data, but distinct differences in larval responses between the control and test streams can be observed nevertheless.

Dicosmoecus gilvipes were not collected for 12 days of rearing in the model streams as was done for *Gumaga nigricula* in Run 1. In Run 4, however, 9 of the 10 *Dicosmoecus gilvipes* larvae initially in the stream were "active" after 9 days. Presumably there were no inherent stresses to the *Dicosmoecus gilvipes* larvae in the other three streams.

Table 4 shows that with concentrations of up to 2% filtered Omega-9 water, no acute toxic responses were observed during the 9 days of exposure. There was a minor trend for prepupae to form with more than 1% of this effluent in the stream water.

In Run 3 unfiltered Omega-9 water was used as the test effluent. As in Run 2, no appreciable decrease in "active" individuals was observed in the streams receiving effluent as compared with the control stream. At the end of day 4 in Run 3 however, there did appear to be a tendency for the larvae in the streams with the higher Omega-9 water concentrations to become inactive. This distinction disappeared by the conclusion of the run on day 9. In contrast to the filtered Omega-9 water run, dead larvae were found at the higher concentrations of effluent.

The synthetic, ammonium carbonate wastewater used in Run 4 corresponds to the ammonium levels found in streams with up to about 2% Omega-9 water concentration. As in Run 2 with these effluent ammonium concentrations, no pronounced difference was observed in the numbers of active *Gumaga nigricula* larvae between the test and control streams of Run 4. This result was expected as the ammonium concentrations used in Run 4 duplicated those of Run 2; however, with Run 4 no other oil shale related constituents were present. At most the synthetic, ammonium carbonate wastewater woudl exhibit a toxic response no greater than that of corresponding dilutions of Omega-9 water, unless the other oil shale effluent components are antagonistic toward salt toxicity. As the Omega-9 water dilutions used in Run 2 were apparently too great to elicit demonstrable reductions in *Gumaga nigricula* activity in 9 days, the ammonium carbonate dilutions of Run 4 similarly proved to be too great.

The *Dicosmoecus gilvipes* larvae that were exposed to the synthetic ammonium carbonate wastewater along with the *Gumaga nigricula* in Run 4 showed a clear sensitivity to the higher concentrations. The streams receiving ammonium carbonate to computed stream concentrations of 2.26 mM and 4.52 mM had significanlty fewer numbers of "active" Dicosmoecus gilvipes larvae than the streams with 0.56 mM and 0 mM ammonium carbonate dilutions. In the two higher concentration streams, a total of six Dicosmoecus gilvipes larvae were missing over the course of the 9-day run as compared with only one larva in the other two streams. Although the precise fate of the missing larvae is unclear, probably they were either prompted to climb up the cage screening above the water line and into the lower reservoir of the stream in an avoidance response, or they were cannibalized by other larvae and their cases used as case maintenance material by the remaining active Dicosmoecus gilvipes larvae. Any larvae climbing into the lower reservoir would be sucked into the recirculating pond and macerated. Although probably the missing larvae should properly be considered as demonstrating a toxic response, particularly since only one missing larvae occurred in the control and low concentration streams, the conclusions drawn from Run 4 remain the same regardless of the disposition of the missing larvae.

Note is made that in Runs 3 and 4 the measured ammonia concentrations deviate markedly from the computed concentrations (Table 2). In Run 2 the correspondence was much closer. A definitive explanation for this deviation awaits further investigation. Several hypotheses are evident, however. It is possible that the primary producer organisms of the aufwuchs communities in the streams selectively shifted to those species favoring ammonia as a nitrogen source over nitrate. In each case the ammonia determinations were made at the end of the run when the aufwuchs biomass was the greatest and had the greatest nitrogen uptake. With this eventuality the ammonia concentrations in the streams would be reduced to the degree that this nutrietn was removed by the aufwuchs biomass. In Run 2 presumably the aufwuchs communities still preferred to meet their nitrogen requirement with nitrate. The reason for any inorganic nitrogen uptake shift by the primary producers is not clear since 1.4 mg/l of nitrate nitrogen was always provided in the makeup water (Table 1). Both ammonia and nitrate are readily utilizable nitrogen sources for most species of algae and both were present in excess of algal requirements in the streams receiving effluent additions. A more probable explanation for the discrepancy between computed and measured ammonia concentrations is nitrification of the ammonia to nitrite and then nitrate by nitrifying bacteria whose growth was favored by the high ammonia levels in the streams. Neither nitrite nor nitrate is measured in teh hypochlorite test for ammonia. This hypothesis would adequately account for the increased divergence of the calculated ammonia concentrations from the measured values in each successive run if the nitrifier activity in the stream systems increased with time. It is also possible that the ammonia was evolved as a gas. However, arguments for this mechanism are weakened by the fact that the lower pH of some of the streams in the last two runs should have prevented ammonia evolution and yet, the large deviations between the computed and measured concentration occurred only in the later runs. The accuracy of the phenolhypochlorite method is supported by the close agreement of the standard curves generated from a stock ammonia solution for each run.

Limitations in the design of this study include the following: (1) too few organisms were involved in the bioassays; (2) a finer discrimination of larval activity responses is necessary, since other more subtle sublethal effects of exposure to oil shale related effluents are ignored by this classification scheme. In terms of this latter point, it should be noted that the *Gumaga nigricula* larvae of the highest effluent concentration streams in Runs 2 and 4 were visibly more sluggish than individuals from the other streams. These larvae exposed to the highest effluent concentrations moved around their cages less and appeared to have difficulty keeping balance and maintaining a grip on the cage screening. Another response resisting description under the current scheme is the phenomenon of case abandonment by the larval caddisflies. Both caddisfly species sometimes left their cases but this occurrence in the *Dicosmoecus gilvipse* larvae was much more common. A system whereby these responses can be quantitatively measured would be preferable to the preliminary methods that we chose.

An appropriate measure of caution must be used in extrapolating laboratory results of effluent studies to those results that would be obtained in natural habitat conditions. The laboratory conditions include elevated temperature, artificial illumination, inorganic nutrient supplementation of the stream water, and possible exposure to exotic sloughed aufwuchs organisms, all of which may significantly affect the response of the organisms under study. Confirmation of the results obtained here by field bioassays must be obtained prior to drawing firm conclusions as to the effect of these oil shale related effluents on aquatic biota.

CONCLUSIONS

1. *Gumaga nigricula* larvae can be maintained in the laboratory model streams with no effluent loading at nearly 100% survival for at least 12 days.

2. Concentrations of filtered Omega-9 water up to 2.12% and unfiltered Omega-9 water up to 1.06% produce no demonstrable reductions in *Gumaga nigricula* "activity" after 9 days of exposure in the model streams.

3. *Gumaga nigricula* "activity" is not notably reduced by rearing in streams receiving up to 4.52 mM concentrations of ammonium carbonate in the makeup water for 9 days.

4. The "activity" of *Dicosmoecus gilvipes* larvae in the laboratory model streams that were fed ammonium carbonate concentrations of 4.52 mM and 2.26 mM is significantly reduced but not at a dilution of 0.56 mM.

5. *Dicosmoecus gilvipes* larvae are potentially more sensitive indicators of environmental stress from ammonia-containing effluents than are *Gumaga nigricula* larvae.

6. This continuous flow bioassay technique has many potential applications in assessing the toxicity of oil shale related effluents.

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BIOLOGICAL MONITORING OF OIL SHALE PRODUCTS AND EFFLUENTS USING SHORT TERM GENETIC ANALYSES

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ABSTRACT

The long term health hazards such as mutagenesis, carcinogenesis and teratogenesis due to the exposure to crude shale oil, particulate pollutants and the leachates from raw or spent shale constitute a major concern in the development of shale oil technology. In order to monitor such biological effects, we have applied short term genetic analyses with the exemplary test materials. The Salmonella/microsomal activation system (Ames assay) was generally applicable but only upon chemical fractionation. The Stedman liquid/liquid extraction procedure or the Sephadex gel filtration (LH-20) technique were effectively utilized. Mutagenicity analyses with various crude oils and product water have revealed biological activity in the basic (aromatic amine fractions) or in the neutral (polyaromatic hydrocarbon fraction) fractions. Extracts and chromatographically isolated materials from raw and spent shale were subjected to mutagenicity studies. Mutagenic activity was noted and correlates with the biological activity of compounds that are either identified or predicted to occur in these materials. Comparison to other energy technologies and overall health hazard of the test materials will be discussed.

INTRODUCTION

The long term health hazards such as toxicity, mutagenicity, carcinogenicity and teratogenicity are of great concern in the development of new alternate energy technologies, including the oil shale industry. Exposure of the personnel in industry as well as consumers to the oil shale deposits, contaminated aqueous effluents and airborne particulates might constitute the biological hazard. In addition entry of the leachates from raw and spent shale into drinking water systems represents another potential route of entry into human environment. Thus, the need for biological monitoring of such processes is obvious and every effort should be made to minimize the toxic and genotoxic effects associated with this industry.

The approach for biological monitoring of the shale oil industry is twofold. (1) Development of an adequate biological testing (quality control) to monitor various processes, effluents or personnel in the development of the engineering and control technology. Various genetic-toxicological test procedures are now available for the detection and isolation of biological hazard. However, it is necessary to identify which of these procedures can be advantageously, appropriately and economically applied (quality control) in determining biological effects. (2) Once the base line biological data is developed, it is necessary to periodically monitor the processes when they are completely developed for full size commercial production.

In order to rapidly and inexpensively ascertain the potential mutagenicity hazards of various test materials, we have examined the feasibility of using short term genetic assays to predict and, in some cases, aid in isolating and identifying chemical mutagens. Furthermore, recent studies[1] have shown that there is an extremely high correlation between the ability of a compound to induce genetic damage and the carcinogenic potential of the compound. Thus, the mutagenicity assay might act as prescreen for carcinogens. In the studies presented here we have used the Ames Salmonela histidine reversion assay[1] to assay the mutagenic potential of chemically fractionated[2] crude shale oil, product water from shale oil process[3] and chromatographically separated leachates and extracts from raw and spent shale.[4]

In order to maintain the uniformity of samples that are tested at various laboratories, the repository[5] at the Oak Ridge National Laboratory, Oak Ridge (supported by the U.S. Environmental Protection Agency), collects and supplies adequate amounts of exemplary materials from the oil shale and other related energy technologies. Materials used in this study were obtained from the ORNL repository and Dr. J.J. Schmidt-Collerus, Denver Research Institute, Denver, Colorado.

MATERIALS AND METHODS

A. Mutagenicity Testing-Methodology

The Salmonella typhimurium strains used in various assays are listed below. All were obtained through the courtesy of Dr. Bruce Ames, Berkeley, California.

TA100 hisG46, uvrB, rfa (missense plus R factor)
TA98 hisD3052, uvrB, rfa (frameshift plus R factor)

In screening of fractionated materials, the two strains TA98 and TA100 were generally employed. Standard experimental procedures have been given by Ames et al.[1] Briefly, the strain to be treated with the potential mutagen(s) is added to soft agar containing a low level of histidine and biotin along with varying amounts of the test substances. The suspension containing approximately 2×10^8 bacteria is overlaid on minimal agar plates. The bacteria undergo several divisions with the reduced level of histidine, thus forming a light lawn of background growth on the plate and allowing the mutagen to act. Revertants to the wild-type state appear as abvious large colonies on the plate. The assay can be quantitated with respect to dose (added amount) of mutagen and modified to include "on-the-plate" treatment with the liver homogenate required to metabolically activate many compounds.

Fractions and/or control compounds to be tested were suspended in dimethyl sulfoxide (supplied sterile, spectrophotometric grade from Schwarz/Mann) to concentrations in the range of 10-50 mg/ml solids. Normally, the fraction was tested with the plate assay over at least a thousandfold concentration range with the two tester strains TA98 and TA100. Revertant colonies were counted after 48 h incubation. Data were recorded and plotted vs added concentration, and the slope of the induction curve was determined (Figure 1). It is assumed that the slope of the linear dose-response range reflects the mutagenic activity. Metabolic activation for procarcinogens was incorporated into the assay by the addition of rat liver microsomal ensymes (liver S-9 mix from rats induced with Aroclor). Routine controls demonstrating the sterility of samples, enzyme or rat liver S-9 preparations, and reagents were included. Positive controls with known mutagens were also included in order to recheck strain response and enzyme preparations. All solvents used were nonmutagenic in the bacterial test system. See Figure 1.

B. Samples-Source

(1) A crude oil sample from the aboveground simulated *in situ* oil shale retorting process; (2) the aqueous product water consisting of the centrifuged water of combustion from the same process (both samples 2 and 3 courtesy of Dr. Ricahrd Poulson of the Laramie Energy Research Center). (3) Carbonaceous spent shale from the TOSCO Process was obtained by the courtesy and cooperation of Colony Corporation (ARCO) and the second from the Paraho (Direct Mode) Pilot processing plant.[a]

C. Chemical Fractionation

(1) Class fractionation scheme: The fractionation technique developed by Swain et al.[2] and modified by Bell et al.[6] was used to fractionate the oil samples and the aqueous samples. The technique involves acid-base separation using liquid/liquid partitioning. The neutral fraction was fractionated into secondary fractions using Florisil column and elution with hexane, benzene, ether and methanol. The acidic and basic fractions were separated into ether or water soluble secondary fractions.

(2) Since acid-base separation technique involves harsh chemical treatment, a much gentler technique developed by Jones et al.[7] using Sephadex LH-20 gel filtration technique was used. The technique utilizes the separation of hydrophilic and lipophilic fractions in Step I, separation of polymeric, sieved and hydrogen-bonding fraction from lipophilics in the Step

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[a] Obtained by Dr. J.J. Schmidt-Collerus.

II and finally separation of aliphatic and aromatic fractions (ring size) from sieved fraction in the Step III.

(3) Extraction of raw and spent shale: each shale sample was Soxhlet extracted for 6 days with benzene and the residue of benzene solubles was then concentrated by distilling off the solvent.[4] The final concentration of the benzene solubles lies in the range of 10-20 mg/ml (a range suitable for TLC separation). Chromatographic separation of the complex benzene extract into polynuclear aromatic hydrocarbons (PAH, neutral), polar compounds (azaarenes, phenols, etc.) and other nonpolar hydrocarbons was achieved by using one-dimensional silica gel thin layer chromatography and was described previously.[4] The saturated hydrocarbons run with the solvent at the top of the plate; PAH's run in a group forming a wide fluorescing band in the top portion of the plate. Polar compounds migrate through the lower half of the plate separating into bands while most polar materials remain at the origin. The PAH residue was subjected to a second separation on a silica gel plate to achieve a higher quality of separation. Separation of the individual PAH compounds was achieved with reasonable success on a two-dimensional mixed thin-layer chromatographic plate.

RESULTS AND DISCUSSION

A. Oil Samples

In the investigation of the feasibility of the coupled analytical mutagenicity assay approach, we examined the mutagenic activity of fractionated in situ retorted shale oil sample (simulated). Each primary fraction was assayed with the Ames strains. The distribution by weight of the test materials, the "specific activity" (revertants/mg) of each fraction, and the contribution of each fraction to the mutagenic potential of the starting material (product of weight percent and specific activity) are listed in Table 1. Data are given for the frameshift strain TA98 with metabolic activation with enzyme preparations from Aroclor 1254-induced rats. The shale oil contained significant activity in the neutral fractions and in other fractions, particularly in the Basic Fraction (B_E, ether soluble). Note that the sum of activities from the neutral subfractions corresponds to the value obtained from the unfractionated neutral material.

Figure 1 shows the dose-response curves for two of the shale oil fractions. The slope of the linear portion of the induction curve represents the revertants/mg of the fraction (specific activity).

Comparable evaluations of crude synthetic fuels from coal liquefaction processes have pointed to consistently higher mutagenic potentials in synthetic fuels than in the materials assayed here.[8]

B. Aqueous Sample

In order to extend the techniques to an aqueous material that might have more environmental importance, we assayed the centrifuged product water from the aboveground in situ retorting process (Table 2). Although a number of highly active materials occur, again in the basic fractions, the overall contribution of the contaminating organic portion appears to be low. Note also that the neutral portion, usually comprised of water insoluble polyaromatic hydrocarbons, contains little mutagenic activity in this aqueous sample.

Since the LH-20 gel filtration technique is a much gentler system, we have examined the feasibility of testing shale oil samples fractionated with LH-20 fractionation scheme. The results are given in Table 3 which shows the general applicability of this technique for biological testing. The activity was recoverable completely (see summation column, Table 3). Total mutagenic activity recovered after fractionation (280 rev/mg) is comparable to the activity obtained with the acid-base fractionation technique (178 rev/mg).

Table 4 lists the results of mutagenicity testing (strain TA98 and TA100, with metabolic activation) with the extracted and chromatographically separated materials from TOSCO II series (CSA II represents test samples from TOSCO process spent shale). The first sample, Diffuse fluorescent material combined (DF COM) was derived from a benzene extract. The sample represents the combined material from 5 TLC plates and is, in general, similar to the neutral or polycyclic aromatic hydrocarbon fraction from acid-base fractionation scheme. The main constituents are probably a homologous series of alkyl substituted and poly-condensed substituted aromatic hydrocarbons. The mutagenicity testing results detect mutagenic activity.

The next samples represent the polar material, from TOSCO II spent shale. The recovered materials are roughly analogous to a basic fraction by the acid-base extraction technique. Predictions would include nitrogenous polycondensed species, acridine, dibenzacridines, along with some acids, phenols and high molecular weight aromatic amines. Mutagenicity can be detected with the Salmonella system. Note in Table 2 that samples D-1135 and D-1165 differ quantitatively and qualitatively. Conceivably, minor changes in the extraction procedures and chromatography can alter the bioassay results.

When the total benzene soluble fraction from Paraho spent shale is analyzed, toxicity masks any mutagenic effect that might be present. However, a similar crude extract from raw shale (APVI^1) air particulate was assayable and mutagenic activity was detectable.

C. Utility of Short Term Tests for Mutagenicity

The use of short term tests for mutagenicity coupled with chemical fractionation and analyses of test materials appears to be a valid research approach. Their utility in predicting potential genetic hazard is obvious. The use of the mutagenicity data as a prescreen for carcinogenesis may also be of value, but probably not in a quantitative sense. Too many factors modify the whole-animal carcinogensis response to expect the type of mutagenicity screening used here to directly reflect the extent of carcinogenic potential.

The biological testing is a complex phenomenon which warrants extreme caution in its application and interpretation. Implication of various genetic and biochemical variables was previously described.[9] The choice of bacterial strain or the inducer involved in metabolic activation could alter the test results. Furthermore, no one short term test should be relied on for testing. Other system[10] might complement one another.

However, in the contest of a prescreen for mutagenesis, and perhaps for carcinogenesis, the testing of crude mixtures with the Ames system is a feasible approach provided that appropriate fractionation, chemical analyses, and validation accompany the bioassays. A more important use of the short term mutagenicity tests may lie in the dissection of a known response in a crude material and the tracing of the effect to the ultimate organic component(s) responsible for the potential damage. The need exists for standardizing test procedures so that they can be routinely utilized for biological monitoring of processes and process streams associated with oil shale technology.

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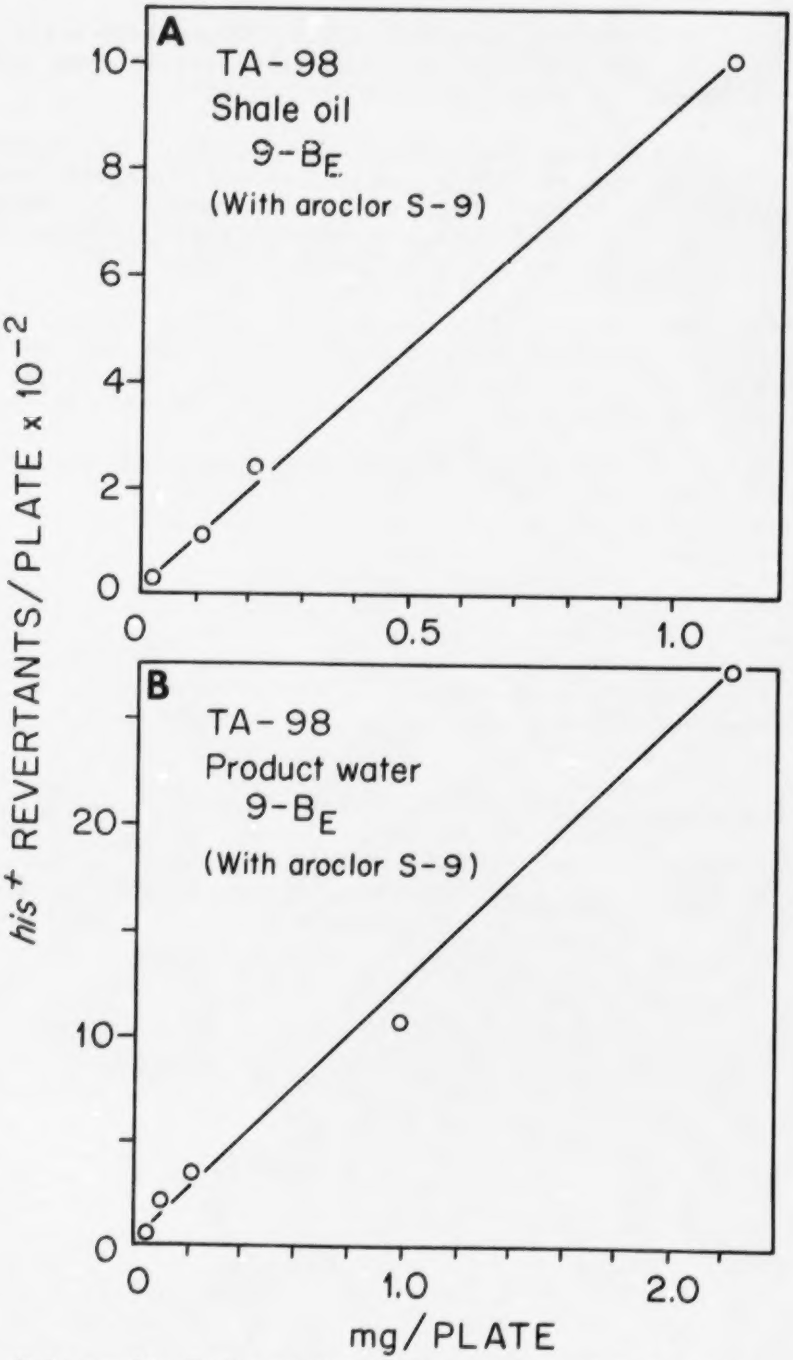

Figure 1. Mutagencity Tests of Crude Oil Sample. (a) From the Aboveground Simulated In Situ Oil Shale Retorting Process and (b) from the Supernatant of Centrifuged Process Water from (a).

TABLE 1

DISTRIBUTION OF MUTAGENIC ACTIVITY IN FRACTIONS OF SHALE OILS[a]

Fraction[b]		Shale Oil		
		Relative weight, % of total	Specific activity, rev/mg[c]	Weighted activity, rev/mg[d]
1. $NaOH_I$		1.02	256	3
2. WA_I		0.05	185	>1
3. WA_E		1.23	52	1
4. SA_I		0.09	0	--
5. SA_E		0.26	159	>1
6. SA_W		0.55	160	1
7. B_{Ia}		0.20	1377	3
8. B_{Ib}		0.26	800	2
9. B_E		7.11	952	68
10. B_W		0.28	223	1
11. Neutral		86.66	112 (109)[e]	97
TOTAL		97.71		178
Neutral subfractions				
Hexane	A	58.69	40	23
	B	2.14	625	13
	C	1.27	750	10
Hexane/benzene	A	4.38	238	10
	B	1.89	340	6
	C	1.39	320	4
Benzene/ether	A	12.43	65	8
	B	2.19	142	3
	C	1.29	253	3
Methanol	A	15.12	179	27
	B	0.49	684	3
	C	0.93	263	2
SUBTOTAL		102.21		112

TABLE 2

DISTRIBUTION OF MUTAGENIC ACTIVITY IN FRACTIONS OF AQUEOUS SAMPLE [a]

	Shale-oil Product Water		
Fraction[b]	Relative weight[c] % of total	Specific activity, rev/mg	Weighted activity, rev/mg
1. $NAOH_I$	--	--	--
2. WA_I	1.5	397	5
3. WA_E	6.3	105	7
4. SA_I	3.9	0	--
5. SA_E	16.8	0	--
6. SA_W	65.0	0	--
7. B_{Ia}	0.1	52	<1
8. B_{Ib}	0.1	1468	1
9. B_E	2.7	1575	42
10. B_W	1.3	868	12
11. Neutral	2.4	52	1
TOTAL			68

Footnotes

[a] All assays carried out in the presence of crude liver S-9 from rats induced with Aroclor 1254.

[b] I = insoluble (fractions a and b), E = ether soluble, W = water soluble, WA = weak acid, SA = strong acid, and B = base.

[c] rev/mg = revertants/milligram (strain TA98). Values are derived from the slope of the induction curve.

[d] Weighted activity of each fraction relative to the starting material is the product of columns one and two. The sum of these products is given as a measure of the total mutagenic potential of each material. The value for the neutral fraction was calculated from the value for the weighted subfractions.

[e] Activity based on assay of the total neutral fraction before chromatography rather than on the summation of the individual subfraction.

TABLE 3

MUTAGENIC ACTIVITY OF SHALE OIL FRACTIONATED WITH SEPHADEX LH-20 SYSTEM

	Specific Activity[a] (rev/mg)	Weighted Activity	Summation of Fractions
1. Original	750	750	
3. Hexane Insol.	1750	23	413
4. Hexane sol.	400	390	
5. Hydrophilic	1400	103	248
6. Lipophilic	175	145	
7. Polymeric	250	6	200
8. Sieved	200	155	
9. H-Bonded	750	39	
10. Aliphatic	0	0	109
11. Mono-aromatic	78	4	
12. Di & Tri-aromatic	800	49	
13. Poly-aromatic	2800	56	
TOTAL		280[c]	

[a] Results obtained with strain TA98 and metabolic activation with Aroclor induced rat liver S-9 mix.

[b] Refer to Table 1.

[c] Summation of fractions 3, 5, 7, 9, 10-13.

FIGURE LEGEND

Figure 1. Induction of revertants in Salmonella strain TA98 with increasing concentration of (A) Fraction 9, basic, ether-soluble from shale oil; and (B) Fraction 9, basic, ether-soluble from product water with activation with an enzyme (S-9) prepared from rat livers induced with Aroclor 1254.

TABLE 4

MUTAGENICITY RAW AND SPENT SHALE

Sample Designation	Fraction Tested	Mutagenicity his$^+$ REV/mg[a]	
		TA 98	TA100
CSA II (1) (TOSCO)	Diffused Fluorescence	220	360
CSA II (1) (TOSCO)	Polar D113S Material D116S	500 320	400 0
CSA II (2) (TOSCO)	Polar D97S Material	220	0
SA VII (1) (PARAHO)	Total Benzene Soluble	Toxic	Toxic
AP VI (1) (PARAHO)	Total Benzene Soluble	60	400

[a] Slope of dose-response curve.

DOSIMETRY OF COAL AND SHALE DERIVED CRUDE LIQUIDS AS MOUSE SKIN CARCINOGENS

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SUMMARY

In a series of three separate experiments mice have been exposed to various concentrations of fossil liquids obtained from coal, oil shale or natural petroleum. All materials were capable of inducing squamous cell carcinoma, however, potency differed substantially. Skin carcinogenicity was markedly greater for both coal and oil shale liquids than was observed with natural petroleums. None of the syncrudes approached the skin carcinogenicity of a pure reference carcinogen, benzo(a)pyrene (BP). It is unlikely that concentration of material in the vehicle applied to the test animal will allow meaningful comparison among the diverse agents of interest to the synthetic fuels industry. To better establish the relationship between actual tissue dose and surface concentration we are investigating various *in vitro* and biochemical measures of hydrocarbon-skin interaction to determine which, if any, could serve as a more definitive measure of surface dose. Results, using BP as a marker carcinogenic hydrocarbon, suggest that carcinogenic crudes inhibit BP metabolism in skin organ culture as well as interaction of BP adducts with epidermal DNA, *in vivo*.

INTRODUCTION

A determination of whether offsite release of liquid or particulates from oil shale production or refining represent any significant health risk to man or his environment is difficult, even for existing well established industries, let alone a new and still experimental oil shale technology. However, the potential long term costs of waiting until the industry achieves self-sufficiency before commencing health effects research provides sufficient justification for a careful and systematic examination of the potential for specific hazards. Our present focus is upon the inplant or worker population who potentially are exposed to process streams, ambient air or end products. For all potential risk scenarios, the one deemed most important on the basis of both historical[1] as well as practical considerations is an assessment of the potential health consequences of intermittant skin exposure.

Possible dermatologic effects represent a continuum, ranging from acute irritation and inflammation to delayed effects such as hypersensitivity and skin carcinogenesis. It is practically and biologically unrealistic and inappropriate to single out any of the discrete components of this complex to the exclusion of all others, but out of practical necessity our experimental emphasis is placed upon the skin carcinogenicity of process materials, with special priority given to the final products. The rationale is that no matter what the technology, its physical location or intended purpose, a product oil will result and eventually enter commerce in one form or another. An understanding of the relative skin carcinogenicities of these materials in experimental animals, coupled with information concerning the underlying basis for demonstrated differences could, if applied judiciously, be of benefit both to the employer and employee as well as the general public. This presentation will describe the approach we have taken to accomplish this objective and will illustrate both the progress achieved as well as the problems which remain.

MATERIALS AND METHODS

SKIN CARCINOGENESIS TESTS

Equal numbers of SPF male and female C3H/fBd mice were distributed five per cage, given free access to pasteurized Purina 5010C and hyperchlorinated-acidified water. Bedding was hardwood chips. Test materials were dispersed or dissolved by brief sonication in a mixed solvent consisting, by volume, of 30% acetone and 70% cyclohexane. Controls were shaved and handled just as treated mice but exposed to the vehicle only. Materials were applied either Monday, Wednesday and Friday or Monday and Thursday depending upon the experiment. Three kinds of experiments have been done. (1) Twenty-two-week, single concentration, three times weekly, followed by a 22-week period without continued treatment to assess the clinical significance of lesions induced during or developing subsequent to the exposure period. (2) Thirty-week exposure at various dose rates, twice weekly with a planned 20-week clinical followup. At present we are 12 weeks into the followup so these data must be treated as preliminary. (3) Twenty-four-month, three times weekly exposure at various dose rates. Fifty microliter of all test materials are applied to the dorsal skin using a micropipette. Evaluation of lesions occurring at the site of application is based upon histologically confirmed squamous carcinoma in the 22-week study. Since the 30-week experiment is still in progress the evaluation of the lesions is dependent upon clinical criteria and therefore must be viewed as preliminary pending eventual histologic confirmation. In the 24-month study animals bearing carcinomas are distinguished on the basis of local extension and infiltration of the tumors into the subcutis.

SAMPLE IDENTITY AND CHARACTERIZATION

The samples tested for sking carcinogenicity have also been compared analytically with respect to constituents assumed to be especially relevant to mammalian epidermal carcinogenesis, type and content of polyaromatic hydrocarbon (PAH). Detailed description of the techniques used and additional sample data can be found elsewhere.[2,3] Briefly, the total wt % PAH was determined by an acid-base solvent partition used extensively in the analytical fractionation of tobacco smoke condensate,[4] benzo(a)pyrene (BP) concentration was determined using quantitative TLC after removing interfering components by gel permeation chromatography.[5]

Experiments have been done using five crude materials, two coal liquids, a shale oil, a composite natural petroleum and Wilmington, California natural crude. Coal liquid A was produced by the synthoil catalytic hydrogenation process and provided through the courtesy of the Pittsburgh Energy Research Center. Coal liquid B was produced by the pyrolytic COED process from Western Kentucky Coal and was provided by the FMC Corporation. Crude shale oil was produced in a simulated *in situ* aboveground retorting of Green River oil shale and was provided by the Laramie Energy Research Center. Natural petroleum has been tested both as a blend and as a single crude. The blend consisted of 20% Wilmington, California; 20% South Swan Hills, Alberta, Canada; 20% Prudhoe Bay, Alaska; 20% Gach Sach, Iran; 10% Louisiana-Mississippi Sweet; 10% Arabian Light. The single source natural petroleum was Wilmington, California. For most experiments materials were solubilized or suspended in a composite solvent, consisting of 70% cyclohexane and 30% acetone, by brief sonication prior to skin exposure. Reference BP (>99% pure) was obtained from Aldrich Chemical Company.

SKIN PAH METABOLISM, *IN VITRO*

It is possible that noncarcinogenic constituents of complex mixtures could influence the metabolic activation and clearance of known active carcinogenic components and thus indirectly contribute to observed differences in potency. One way to determine whether this occurs and to what extent materials differ is to compare the skin's metabolism of tritiated benzo(a)pyrene in the presence and absence of various amounts of crude. This is accomplished by floating measured pieces of intact mouse skin on a buffered physiologic solution, incubating the skin and observing the extent to which tritium applied to the exterior surface is converted to metabolites soluble in the aqueous phase in contact with the subcutis.

MEASUREMENT OF B(A)P BINDING TO TARGET TISSUE DNA

As a further measure of the presence of constituents that alter the penetration or metabolism of known carcinogenic PAH, known amounts of tritiated BP are added to the undifferentiated crude mixtures. The spiked crudes are applied to mice and at various times mice are killed, the skins excised and the epidermis separated by brief heat treatment. The epidermis was subsequently homogenized and the DNA isolated and purified.

In addition to the radiometric method, fluorescence characteristic of BP adducts bound covalently to DNA was also determined. For these measurements the DNA recovered from a single animal (~100 ug) was dispersed in a volume of 0.15 ml, taken up in 3 mm ID Quartz tubes and fluorescence determined at 77°K. The excitation and emission monochrometers were set 28 nM apart; by scanning both monochrometers simultaneously a spectrum is obtained which is selective for BP and minimizes contributions from nonstructured background emissions.

RESULTS

SKIN CARCINOGENICITY

Table 1 lists the results obtained when materials are applied three times weekly for 22 weeks followed by a 22-week holding period to allow lesions to progress without continued insult. These data together with additional characterization appear in greater detail elsewhere.[6] Under these conditions all the syncrudes are capable of evoking squamous epidermal tumors that are both histologically and biologically malignant. Under identical conditions of exposure no skin neoplasms were observed in mice exposed to the composite petroleum.

The data presented in Table 2 represent the status of an experiment still in progress. At this time the animals have completed 30 weeks of twice weekly exposure and are 12 weeks into the clinical observation period. The most striking difference between this and the preceding study was a sharply reduced effect observed overall. It is presumed that this was the result of a lower frequency of application.

Table 3 summarizes the results of 24 months, three times weekly application of these materials at low dose rate. Once again, the same relative differences were observed among the various materials, however the longer exposure duration permitted carcinoma induction to be observed in animals treated with the composite natural petroleum. The lethality of the skin tumors is clearly reflected by the correlation between tumor incidence and percent mortality across all groups.

In order to place the preceding data into perspective it is useful to compare the carcinogenicity of the various crudes with that of BP applied three times weekly in the same solvent to the same inbred strain. These data are summarized in Table 4. The BP dose which came closest to approximating the response obtained with the most carcinogenic syncrude was 50 micrograms. It is instructive to note that this is 1/500th the amount of coal liquid A required to elicit a comparable skin tumor incidence.

PAH AND BP CONTENT OF SAMPLES

Table 5 compares the wt % PAH found in each material as well as the approximate concentration of BP in the whole sample. It could be significant that while total PAH content appears not to be correlated with carcinogenicity, the concentration of BP agrees well with the potency of the whole mixture. The limited number of samples precludes assumption of any precise mathematical correlation, however, it will be of interest to compare other crudes on the basis of BP content and observe how well the correlation holds and under what circumstances it fails.

Table 1. SKIN CARCINOGENICITY OF SYNCRUDES ASSESSED BY 3 TIMES WEEKLY APPLICATION FOR 22 WEEKS

Material	Dose/application (mg)	Number	Final % Carcinoma	Average latency	Mortality through 44 weeks
Coal A	25	30	63	149± 8	20
Coal B	25	30	37	191±14	3
Shale oil	25	30	47	154± 9	37
Composite petroleum	25	30	0	0	0

Table 2. SKIN CARCINOGENICITY OF SYNCRUDES ASSESSED BY 2 TIMES WEEKLY APPLICATION FOR 30 WEEKS

Material	Dose/application (mg)	Number	Interim % carcinoma	Average latency	Mortality at 42 weeks
Coal A	25	20	75	206	10
	12	20	35	222	0
	6	20	1	247	5
	3	20	0	-	0
Coal B	25	20	0	-	0
	12	20	0	-	5
	6	20	0	-	0
	3	20	0	0	5
Shale oil	25	20	35	208	5
	12	20	5	213	0
	6	20	0	-	0
	3	20	0	-	0
Wilmington, California	25	20	0	-	0
	12	20	0	-	0
	6	20	0	-	0
	3	20	0	-	0

Table 3. SKIN CARCINOGENICITY OF SYNCRUDES ASSESSED BY 3 TIMES WEEKLY APPLICATION FOR 24 MONTHS

Material	Dose/application (mg)	Number	Final %[1] carcinoma	Average[2] latency	% Mortality at 24 months
Coal A	1.0	50	92	498(10)	78
	0.3	50	26	569(18)	38
	0.2	50	8	653(19)	36
	0.04	50	4	680	26
Coal B	0.8	50	8	565(54)	44
	0.3	50	4	668(8)	36
	0.17	50	2	588(94)	46
	0.03	50	2	679	44
Shale oil	2.5	50	90	483(15)	64
	0.5	50	2	315	40
	0.3	50	2	611	38
	0.1	50	0	-	20
Composite Petroleum	2.0	50	8	658(22)	20
	0.4	50	0	-	26
	0.3	50	0	-	22
	0.08	50	0	-	30
Vehicle	-	50	0	-	28

[1] Uncorrected for intercurrent mortality.

[2] Days (±S.E.).

Table 4. SKIN CARCINOGENICITY OF BENZO[A]PYRENE APPLIED THREE TIMES WEEKLY FOR 24 MONTHS

Dose/application (mg)	Number	Final %[1] carcinoma	Average[2] latency	% Mortality[3] at 24 months
0.050	50	100	139(4)	-
0.010	50	100	206(7)	-
0.002	50	90	533(5)	58

[1] Uncorrected for intercurrent mortality.

[2] Days (±S.E.)

[3] Not calculated in higher dose groups, which were terminated when the tumor response saturated.

Table 5. WEIGHT PERCENT PAH AND CONCENTRATION OF BENZO[A]PYRENE IN SYNCRUDES AND NATURAL PETROLEUMS

Material	Wt. % PAH	ug BP/gm
Coal A	5.1	79
Coal B	6.0	12
Shale oil	2.0	20
Composite petroleum	2.6	∿1
Wilmington petroleum	n.d.	1

BP METABOLISM IN SKIN ORGAN CULTURE

Figure 1 shows the effect of various amounts of crude petroleum on the extent of BP metabolism by skin maintained in organ culture. As can be observed, the more carcinogenic the crude the more BP metabolism is inhibited. It is known, at present, whether this inhibition is a result of direct cytotoxicity or metabolic competition.

BINDING OF BP ADDUCTS TO MOUSE EPIDERMAL DNA *IN VIVO*

There are data suggesting that the degree of covalent interaction between specific hydrocarbon metabolites with one or more DNA nucleosides within target tissue DNA is highly correlated with the mutagenicity and carcinogenicity of pure PAHs.[7,8,9] Assuming that this correlation will hold for a broad range of structurally related components of complex mixtures we are developing assay techniques that will allow a precise determination of the time integrated dose of material that interacts with epidermal DNA following topical application *in vivo*.

Figure 2 contrasts the kinetics of BP adduct formation and removal or dilution over a 28-day period. Each data point consists of the pooled epidermal DNA obtained from three mice treated topically at time zero with 250 uC BP in a volume of 0.1 ml acetone. Cold BP, 80 ug, was added as carrier. The results show that binding occurs almost immediately and reaches a maximum at approximately 24 hours followed by a gradual decrease. It is unknown to what extent the decrease is due to specific repair processes or simple dilution of the label by cell division.

Figure 3 demonstrates the efficacy of the fluorescence method for detection of BP adducts bound to DNA. The open circles represent the extent of binding obtained as a function of BP dose using tritiated BP; the solid circles reflect the relative specific fluorescence intensity in the same DNA samples. While the data points are few there is good agreement between the two measures of BP-DNA interaction. The data further show that the correlation between the amount of BP applied to the skin and that associated with DNA is essentially linear through 400 ug.

The influence of the various syncrudes and natural petroleum on BP-DNA binding *in vivo* is given in Table 6. These data agree with evidence obtained in skin organ cultures (Figure 1) that the more carcinogenic the material the greater the inhibition of BP binding to epidermal DNA *in vivo*.

DISCUSSION

The data presented reveal wide differences in the skin carcinogenicity of synthetically derived hydrocarbon mixtures. The observed association between concentration of BP in the parent crude and skin carcinogenicity may be more apparent than real; however, the observation should provide an incentive to compare a wide range of materials on this basis.

TABLE 6. THE INFLUENCE OF SYNCRUDES ON THE RELATIVE BINDING OF TRITIATED BP TO EPIDERMAL DNA IN VIVO

Material	Moles of BP per 10^7 Nucleotides		
	2	20	200 ug[1]
Coal A	9.1	7.9	6.1
Coal B	6.6	5.2	4.3
Shale Oil	7.0	5.2	4.1
Wilmington Petroleum	5.1	4.8	4.7

[1] Amount of crude applied in 0.1 ml of hexane in the presence of 250 uCI (2.5 ug) tritiated benzo(a)pyrene.

Obtaining an integrated measure of "PAH" dose, at the molecular level, may be feasible based upon radiometric or fluorimetric observation of target tissue nucleotides which serve as traps for reactive metabolites generated from complex mixtures in vivo. By routinely conducting these measurements for any materials subjected to empirical whole animal carcinogenesis dose response tests it may be possible to develop sufficient data base to permit this measure to serve as a rapid, inexpensive and quantitative screen for potential skin carcinogenicity.

Given the chemical complexity of syncrudes it is unrealistic to expect that any single measure will suffice to predict carcinogenicity in vivo. There simply are too many parameters involved including initial penetration of the skin lipid barrier, metabolic conversion of various constituents to reactive intermediates, molecular repair and cellular recovery mechanisms as well as systemic hormonal and immunologic factors. In our opinion the only way that experimental animal data can be used in an interpretive, quantitative and predictive way is to better understand the relative importance of each of these factors. With this information, combined with data concerning detailed structural and functional differences between mouse and human skin, we may be in a position to derive quantitative interspecies risk estimates.

ACKNOWLEDGEMENTS

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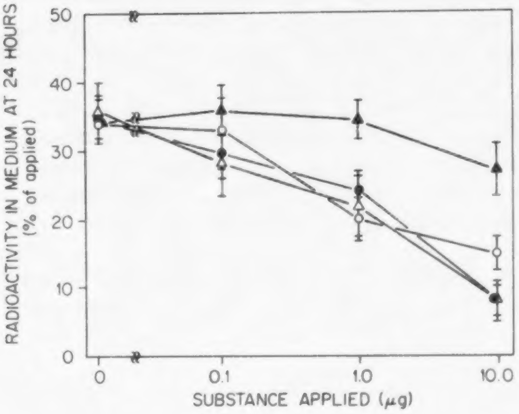

Fig. 1. Relative amount of tritiated BP in medium at 24 hours in the prescence of various material. Coal liquid A (0), coal liquid B (0), Wilmington Petroleum (Δ), shale oil (Δ). Bars represent the standard error.

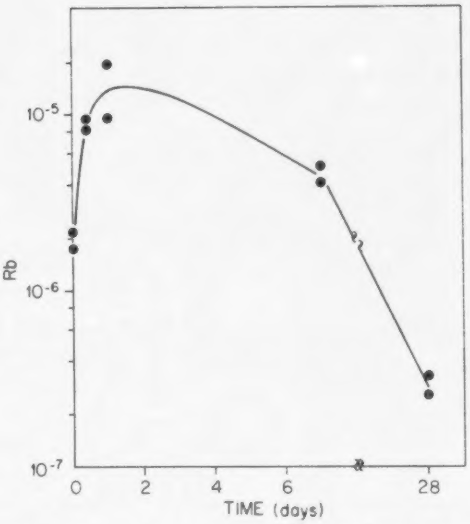

Fig. 2. Kinetics of tritiated BP binding to mouse skin epidermal DNA *in vivo*. Rb (relative bindings) equals the moles of BP bound per mole of DNA nucleotide.

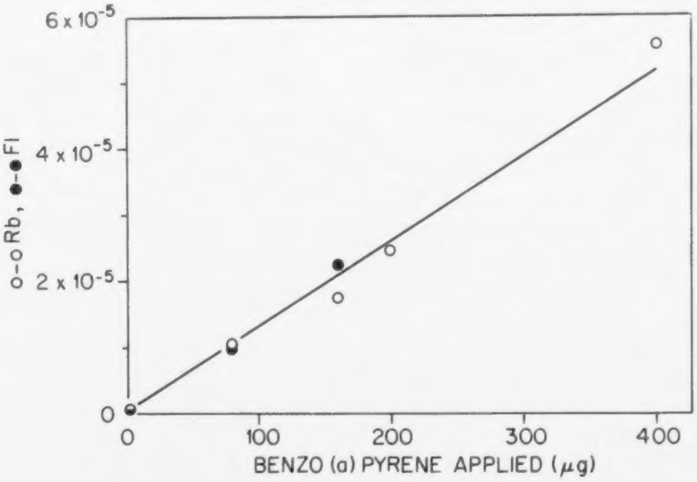

Fig. 3. Dose response relationship obtained for BP binding to mouse epidermal DNA *in vivo* as determined by DNA associated tritium counts (Rb) or relative fluorescence intensity (Fl).

THE CARCINOGENICITY OF VARIOUS SHALE OILS AND SHALE OIL PRODUCTS

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ABSTRACT

Initial studies of workers involved in the production and use of Scottish shale oil revealed an increased incidence of cancer. Subsequently, other studies reported that prolonged exposures to shale oil can indeed produce skin cancer in humans. This fact and the likelihood that the nation will utilize one of its most abundant energy resources, oil shale, dictate that an assessment of the potential health effects of American shale oil and shale oil products should be investigated.

We have investigated the potential carcinogenic potency of several raw shale oil samples produced from various retort methods. In addition to the raw shale oils, we have also studied the carcinogenic potency of several raw shale and processed or spent shale samples. This presentation reports the results of prolonged and repeated applications of these materials to the skin of mice.

INTRODUCTION

Studies of Scottish workers involved in the production and use of shale oil revealed an increased incidence of cancer. It is well known from the reports of Bell[1] (1876) and Scott[2] (1923) that prolonged exposure to shale oil can produce skin cancer in humans. These reports, as well as reports of others, dictate that an assessment of the potential health effects of shale oil and shale oil products should continually be made as new technologies are developed.

As great emphasis is being placed on developing domestic energy sources, it is likely that not only new technologies will be utilized in this endeavor, but also new sources of energy will be used. One such source is oil shale. The elevated temperatures necessary for various retort methods to extract oil from oil shale are likely to produce many organic compounds. Some of these compounds may be carcinogens, co-carcinogens, or promotors and could be present in both the crude shale and the processed or spent shale. To insure protection of the worker who may come in contact with these products, it would be prudent to evaluate the carcinogenic potential of these materials.

Like other investigators, we have reported the benzo(a)pyrene (BaP) content of test materials. This practice was predicated on the early belief that since BaP was present in coal tar, it might also be present in other carcinogenic materials such as crude shale oil. Although many investigators studied the carcinogenic constituents of shale oil during the 1930s, it wasn't until 1943 that Berenblum and Schoental[3] identified BaP in Scottish shale oil. In addition, they also observed a fraction of shale oil to be carcinogenic that did not contain detectable quantities of BaP. Later Hueper and Cahnman[4] (1958) and Bogovsky[5] (1962) reported BaP free American and Estonian shale oil, respectively, to be carcinogenic in mouse skin painting studies. It would behoove toxicologists to perform biological testing to go along with chemical analyses in evaluating the potential hazards of these complex mixtures.

MATERIAL AND METHOD

The following materials were evaluated for their carcinogenic potential in mouse skin painting studies: four crude shale oils which represent two Paraho processes (direct mode and indirect mode), the Union B process and a Colony semiprocess; three raw shales and four spent shales, all provided as finely ground materials.

Young adult C3H/HeJ male mice were treated twice weekly with 50 mg of the test material. The material was applied to the interscapular area of the shaven backs with a microliter pipette or a calibrated dropper. The raw and spent shales were suspended in noncarcinogenic white mineral oil (U.S.P.) in 1:2 ratio (by weight). Mice were treated for 80 weeks or until the appearance of a papilloma. If a papilloma progressed and was diagnosed grossly as a carcinoma the mouse was killed and autopsied. However, if the papilloma regressed the treatments were resumed. In addition to the test groups, the study included two negative and two positive control groups. One negative control group received no treatment, while the other received 50 mg of mineral oil twice weekly. The two positive control groups received 50 mg twice weekly of solutions of BaP in mineral oil at concentrations of 0.15 and 0.05%.

At autopsy all the mice were examined grossly for skin tumors. If tumors were observed, a description, size measurements, and location were recorded on the autopsy record. Skin from the total treatment area of each mouse, as well as other tissues, were submitted for histological examination. This presentation will report only the results of microscopic examination of the skin.

RESULTS AND COMMENTS

A summary of the results of repetitive application of shale oils, raw, and spent shales upon the skin of mice can be seen in the tables that follow. Given in Table 1 are the tumor incidence and the average time at which tumors appeared in the experimental groups receiving the four shale oils and two concentrations of BaP. It can be seen that about 80% of the animals treated with the shale oils developed neoplasms while almost 100% of the mice treated with BaP developed tumors. The average latent periods of the mice treated with the oils are similar to the mice receiving the high positive control (0.15% BaP). The biological activities induced by these oils could not be attributed to their BaP content since they range from 0.00018-0.00042%. Although the tumors recorded in Table 1 were gross observations, they agree very well with the microscopic examinations. The number of mice, observed grossly, having tumors was 225. Two hundred and sixteen of these were confirmed histologically. Six of the remaining nine were not examined microscopically because of postmortem changes.

In Table 2 are the tumor incidence and latent period of various complex mixtures after topically applying them to the backs of mice. Of note is the biological activity exerted by the three shale oils, while no activity was seen among the petroleum crude oils.

Table 3 gives the carcinogenic potency of a sample of raw and upgraded shale oil. It can be seen that upgrading the oil reduces its biological activity. The raw shale oil induced tumors in 86% of the surviving mice while the upgraded oil induced 13%.

Table 4 lists the various neoplasms resulting from topical applications of shale oils and BaP to the skin of mice. The first three types of tumors, fibrous papilloma, squamous papilloma, the keratoacanthoma are benign, whereas the latter two, squamous cell carcinoma and fibrosarcoma are malignant. All the malignant neoplasms induced by the BaP were epithelial in origin, namely, squamous cell carcinomas. The BaP-induced malignancies differ from the shale oil-induced tumors in that all four shale oils also initiated the development of sarcomas. The number of mice developing sarcomas was relatively small, although significant.

The fact that the shale oils stimulated manifestation of fibrosarcomas, suggest that some components of shale oil affect the fibrous tissue of the dermis. This is further substantiated by the occurrence of fibrous tissue papillomas, which is relatively rare in mice treated with BaP. Another fact that may have contributed to the induction of sarcomas was that all of the oils were ulcergenic and depilatory.

Table 5 lists the still-in-progress groups of negative controls, raw, and spent shales. After 80 weeks of topical applications of these materials to the backs of mice and 6 weeks of post exposure, no skin tumors have been observed in any of the animals. The lack of biological activity in the oil shale groups can be attributed to (1) the relatively low concentration of polycyclic hydrocarbons (<0.00001% BaP), (2) that these compounds are very tightly bound to the particulate material and, therefore, no skin absorption, (3) that very little of the raw and spent shale remained in the skin for any length of time.

Although the preceding data apply to C3H mice, it should arouse awareness of the possible hazard that may be associated to human exposure to these oils. New technologies should be monitored or evaluated for their potential health effects on workers who may be exposed.

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TABLE 1

TUMOR INCIDENCE AND LATENT PERIOD AFTER TOPICAL APPLICATION OF SHALE OILS TO MICE

Sample Number	Number of Mice	Final Effective* Number	Number** with Tumor	Average Latent Period (Weeks)
RO-1	50	42	34	31.9
RO-2	50	43	35	21.6
RO-3	50	46	40	28.5
RO-4	50	48	39	25.7
BaP 0.05%	50	48	47	37.8
BaP 0.15%	30	30	30	27.4

*Gross Observation

**Final Effective Number is the number of mice alive at the time of appearance of the median tumor plus those mice that may have died with tumors.

TABLE 2

TUMOR INCIDENCE AND LATENT PERIOD AFTER TOPICAL APPLICATION OF VARIOUS COMPLEX MIXTURES TO MICE

Sample	Number of Mice	Number of Mice Developing Tumors		Average Latent Period (Weeks)
		Papillomas	Carcinomas	
Shale Oil 1 (Heat Transfer)	20	1	17	43±4
Shale Oil 2 (Heat Transfer)	30	1	18	36±2
Shale Oil 3 (Direct Combustion)	30	3	22	43±5
Crude Oil 1 (Texas)	20	0	0	-
Crude Oil 2 (Asphaltic)	20	0	0	-
Paraffinic Distillate (Uncracked Crude)	30	4	2	64±6
Industrial Fuel Oil	20	1	18	17±2
Residuum (Catalytically Cracked)	30	0	30	8±1
0.005% Benzo(a)-pyrene in Toluene	50	6	1	80±8
0.2% Benzo(a)-pyrene in Toluene	30	3	27	31±4

TABLE 3

CARCINOGENIC POTENCY OF RAW AND UPGRADED SHALE OIL

Sample	Number of Mice	Final* Effect Number	Number of Mice Developing Tumors		Average Latent Period (Weeks)
			Malignant	Benign	
Raw Shale Oil	50	45	21	18	30
Upgraded Shale Oil	50	39	3	2	49
Positive Control 0.05% BaP in Toluene	100	92	75	9	46
Negative Control Toluene Only	100	91	0	0	-

*Final Effective Number is the number of mice alive at the time of appearance of the median tumor plus those mice that may have died with tumors.

The number for the Solvent Control is the number of mice alive after one year.

TABLE 4

TUMORS RESULTING FROM TOPICAL APPLICATION OF SHALE OILS TO C3H/HeJ MICE

	Fibrous Papilloma		Squamous Papilloma		Kerato-Acanthoma		Squamous Carcinoma		Fibro-Sarcoma	
Sample Number	No. of Animals	No. of Tumors	No. of Animals	No. of Tumors	No. of Animals	No. of Tumors	No. of Animals	No. of Tumors	No. of Animals	No. of Tumors
RO-1	6	7	9	12	10	13	8	10	6	7
RO-2	5	8	8	14	13	19	15	24	8	9
RO-3	3	3	9	12	16	21	17	23	6	6
RO-4	6	8	12	18	17	24	15	20	5	5
BaP 0.05%	2	2	10	17	22	36	30	35	0	0
BaP 0.15%	0	0	8	16	15	20	25	36	0	0

TABLE 5

TUMOR INCIDENCE AND LATENT PERIOD AFTER TOPICAL APPLICATION OF RAW AND SPENT SHALES

Sample Number	Number of Mice	Final Effective Number	Number* with Tumor	Average Latent Period (Weeks)
Raw Shale 1	50	In Progress**	0	-
Raw Shale 2	50	In Progress**	0	-
Raw Shale 3	50	In Progress**	0	-
Spent Shale 1	50	In Progress**	0	-
Spent Shale 2	50	In Progress**	0	-
Spent Shale 3	50	In Progress**	0	-
Spent Shale 4	50	In Progress**	0	-
Control No Treatment	50	In Progress**	0	-
Control Mineral Oil	50	In Progress**	0	-

*Gross Observation

**After 86 Weeks Duration

CHROMOSOME ABERRATIONS AND LOSS OF SOME CELL FUNCTIONS FOLLOWING *IN VITRO* EXPOSURE TO RETORTED OIL SHALE

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ABSTRACT

An investigation of cellular level effects of processed oil shale from a simulation of modified *in situ* retorting was undertaken as part of an assessment of the toxicity and mutagenicity of oil shale. Complete assessment of the health hazards associated with physical contact, inhalation or ingestion of oil shale has not been examined in humans and until it becomes practical to assess these hazards in man, we must rely upon well-established *in vitro* detection procedures in addition to whole animal testing. CHO cells and L-2 rat lung epithelial cell lines were exposed *in vitro* to processed oil shale particles at different intervals following exposure. Cells were analyzed for chromosome alterations, cell colony forming ability, DNA synthesis and cell transformation. The results of these studies demonstrate that retorted oil shale, under these experimental conditions, does modify cells *in vitro*. Chromosome aberrations increased with dose, cell colony forming ability decreased exponentially with dose, and the rate of DNA synthesis was affected, however cell transformation was not demonstrated after 3 months. Further studies are in progress. (This work was performed under the auspices of the U. S. Department of Energy.)

INTRODUCTION

There is concern over potential health hazards from pollutants formed as byproducts in commercial production of energy. As the technology for processing new sources of energy becomes available, a variety of exogeneous agents will be introduced into the industrial environment which may be implicated in the etiology of occupational diseases, primarily lung ailments.

One potential source of energy currently under development is oil shale, which if commercially produced may raise industrial health questions. Some of the materials of concern are the polycyclic aromatic hydrocarbons and other organic compounds, organo-metallic compounds, trace metals, raw and processed shale, liquids and vapors, and other crude products.

Complete assessment of the health hazards associated with inhalation, ingestion or physical contact with spent oil shale has not been examined in humans and until it becomes practical to perform these studies in man, we must rely on well-established detection procedures devised and refined by many researchers in a variety of _in vitro_ and _in vivo_ methods. Toxicological studies of oil shale can be assessed by _in vitro_ methods in a way not feasible in an _in vivo_ system. Therefore, we have undertaken a study to determine the effects of spent oil shale on cells growing _in vitro_. Three biological parameters which are important for survival, reproductive integrity (colony forming ability), chromosome stability, and DNA synthesis, were examined. These experiments will form a background against which the action of spent oil shale _in vivo_ could perhaps be viewed with respect to lung tissue.

The results of these studies demonstrate that spent oil shale, in the form used and under the conditions of these experiments, does modify cells in an _in vivo_ system.

METHODS

CELL LINES

Two established cell lines which grow as monolayers in culture were used to evaluate the _in vitro_ effects of the action of spent oil shale. The cell lines employed for different aspects of this study were CHO (Chinese hamster ovary fibroblasts) and L-2 (Fischer rat lung epithelial cells). The CHO line was obtained from Puck[2] in 1962 and has been maintained and characterized at Los Alamos Scientific Laboratory by Deaven.[3] It has a near-diploid stemline of 21 chromosomes and for these experiments the cells were grown in Ham's F-10 medium (Microbiological Association, MBA), containing 50 units/ml Penicillin G potassium and 40 μg/ml Streptomycin sulfate. The L-2 cell line was obtained from Kaighn[4] at the 16th passage and at the time of these experiments had a modal chromosome number of 68. When the cell was cloned in culture it was characterized as a type II pneumonocyte.[5] This cell line was maintained on a medium modified by Kaighn[5] and designated F-12K medium (GIBCO), 15 percent fetal bovine serum (MBA), 50 units/ml Penicillin, and 50 μg/ml streptomycin.

OIL SHALE

The retorted oil shale was obtained from Laramie Energy Technology Center (LETC) after simulated _in situ_ processing in a 150 ton retort. The shale was ball-milled to a dust ranging in size from 1.5-20μ, with the majority of the particles between 6-10μ. For use in culture, the shale was concentrated in a slurry in about 0.3-0.5 ml dimethylsulfoxide (DMSO) and diluted with 0.8 percent NaCl for sterilization by autoclave. Further dilutions were made in the appropriate media for adding to cultures. The oil spent shale in media was added to cultures immediately following the plating of cells. The pH of the media was not changed more than 0.4 on the pH scale.

CHROMOSOME ANALYSIS AND PULSE LABELING WITH TRITIATED THYMIDINE

Cell suspensions, in their appropriate media, were inoculated into plastic T-25 flasks (Costar) at a concentration of 1 x 10^6 cells for chromosome analysis and pulse labeling studies. Oil shale (0.05 - 0.15 mg/ml) was added to three flasks for each dose following the inoculation of cells. The flasks were then incubated under 5 percent CO_2 and air at 38°C in a humid atmosphere. Chromosome and DNA synthesis analyses were performed at 16, 22, 46, and 70 hours following treatment, and at these designated time periods, 0.1 μg/ml Colcemid (GIBCO) was added to each flask during the final 3 hours of incubation to block cells in division at metaphase. Twenty minutes prior to fixing cells, tritiated thymidine [^{3}H] TdR, in a concentration of 0.75 μCi/ml, was added to each flask to radioactively label DNA in the cells. Both chromosome analyses and labeling assessment were performed on cells which had been pooled from three flasks; however, separate slides were prepared for each. Chromosome spreads were made after the cells were treated with Colcemid, placed in warm hypotonic KCL (0.075) for 15 minutes at 38°C, and fixed in three changes of fresh cold fix, consisting of one part glacial acetic acid and three parts absolute methanol, at 4°C for about an hour. When the last fix was decanted, the cells were dropped from a micropipette onto chemically cleaned microslides which were removed from chilled distilled water (4°C). The metaphase chromosomes spread on the wet slides after dropping, and to enhance the spreading, the slides were air dried by waving the slides in front of a hair dryer at 58°C for 1/2 minute. They were stained with 4 percent Gurr Giemsa Stain (Improved R66) for 5 minutes. Between 100-200 V metaphase spreads (50 per slide) of good quality were analyzed for chromosome aberrations for each dose level.

Autoradiography was performed on cells which had been pulsed labeled with [^{3}H] TdR to determine the labeling index. For this analysis cells from fixative were dropped onto microslides and air dried. The slides were dipped in Kodak Liquid emulsion (NTB) which had previously been diluted with equal parts of distilled water, and then stored in black slide boxes with a drying agent at 4°C for 7-10 days before developing with D19 developer and staining with 1 percent Gurr Giemsa. For each dose, and subsequent time interval, 500 cells were scored for incorporation of [^{3}H] TdR into DNA.

CELL SURVIVAL

Cell survival was studied by exposing single cells in culture to various doses of oil shale and scoring for visible cell colonies after a suitable period of incubation with the spent oil shale and subsequent removal of the agent. Spent oil shale (0.05-0.3 mg/ml) was added to plastic petri dishes (60 mm, Lux) which had previously been seeded with about 200 single cells. After an incubation period of 6 days with spent oil shale suspension the spent oil shale was removed and the petri dishes were washed three times with Hank's balanced solution (GIBCO). Fresh media was then added and the dishes were allowed to incubate 10 days at which time the cell colonies were fixed and stained with 1 percent Gentian Violet. Colonies containing 50 or more cells were scored and the mean number of 3-5 replicate dishes was determined. A survival curve was determined from the mean number of colonies formed from the single cells following treatment. Two or three experiments of the same type were performed at different times and the results were very similar, therefore, only one survival curve will be shown for the CHO or L-2 cell lines.

RESULTS

CELL SURVIVAL

The response of cells to spent shale suspensions was studied by exposing single cells in culture to various concentrations of shale for 6 days, and scoring for visible cell colonies 1 week following the removal of spent shale. Colony surviving fraction is plotted as a function of dose. The survival curves for the cell lines CHO and L-2 are shown in Figure. 1. The colony surviving fraction for both cell lines shows an exponential response resembling that of a single-hit kinetics[6] with an extrapolation number very close to one. The mean lethal dose or the percentage necessary to reduce survival to 50 percent (LD_{50}) was 0.33 mg/ml for CHO cells and 0.14 mg/ml for L-2 cells indicating that the L-2 (rat lung epithelial cells) were more sensitive to the spent shale than CHO (Chinese hamster ovary fibroblast cells).

DNA SYNTHESIS

CHO cells were pulsed labeled for 20 minutes with [^{3}H] TdR before the end of exposure to spent shale. The percent of cells incorporating [^{3}H] TdR is plotted as a function of the duration of oil shale in Figure. 2. The labeling index of the control cells was between 52 percent and 62 percent over a 44 hour period. The treated cells (all doses) showed a decrease in incorporation of [^{3}H] TdR at 17 hours and reached a plateau at 21 days; thereafter, no further decrease was seen. There was a significant difference between the control and treated cells; and between the lowest dose (0.5 mg/ml) and the two higher doses (1.0-1.5 mg/ml), but no difference between the two. It was interesting that the reduction of DNA synthesis to 40 percent at 24 hours for the treated cells did not go below this fraction at 48 hours, indicating that there may be two cell types, one sensitive and the other insensitive to oil shale. The suppression of DNA synthesis was significant but the degree of suppression was not as great as one encountered with radiation and radiometic drugs. It was noted that the rate of DNA synthesis was somewhat reduced among the treated cells, as measured by grain counts, and the reduction was related to dose.

CHROMOSOME ABBERRATIONS

The scoring of chromosome aberrations were analyzed on CHO cells in metaphase after the cells were exposed to oil shale for 16, 22, 46, and 70 hours. The frequency of aberrations is plotted against the duration of shale treatment in Figure. 3. The peak of aberration frequency for the two higher doses occurred at 16 hours and was 13 percent at 0.15 mg/ml and 9.5 percent at 0.10 mg/ml. There was a 2-2.5 fold decrease in frequency at 22 hours and thereafter, very little or no significant change in the slope of the curves. At the lowest dose (0.05 mg/ml) the peak (6 percent) was not reached until 22 hours after treatment and the curve remained the same at 46 hours, and by 70 hours the frequency had returned to control values. The accumulated data for chromosome aberrations were combined over the 70-hour exposure period and were plotted as a function of dose in Figure. 4, and the accumulated data for the frequency of cells with aberrations over the same period were also plotted as a function of dose in Figure. 5. In both cases, the dose response curves were linear indicating that chromosome aberration frequency and cells with aberrations were dose dependent. Chromosome aberrations produced in CHO cells vary both in type and frequency. Some of the types observed are shown in Plate 1; (a) centric fusion, (b) chromatid deletion, (c) dicentric, and (d) badly damaged chromosomes. Not shown were isochromstid deletions, exchanges and translocations. There were an abnormal number of centric fusion types (a) where the centromeres appeared to be affected and two chromosomes fused at this junction. There was an exponential increase from 1 percent at control levels to 9.5 percent at the highest dose (0.15 mg/ml) of spent shale. Polyploid cells for all doses increased 2-2.5 fold over controls, but the increase was not exponential.

In one experiment with human cells, lymphocytes (leucocytes) from blood were grown in culture and exposed to spent shale (0.5-2.0 mg/ml) for 46 or 67 hours before chromosome preparations were made. Metaphase cells were scored for chromosome damage and the frequency of chromosome aberrations is plotted as a function of dose in Figure. 6. There is a linear dose response to spent shale between 1.0 and 2.0 mg/ml. There were very few chromosome aberrations 46 hours following treatment.

Sister chromatid exchanges (SCE) were investigated in L-2 cells after spent shale treatment. The cells were exposed to shale at the beginning of the culture period and about 48 hours later, chromosome preparations were made and SCE were scored. Table 1 represents the frequency of SCE following 0.10 mg/ml oil shale. The data show that spent shale was effective in increasing the production of SCE over controls and the SCE/chromosome was significantly higher in the treated compared to the controls.

TABLE 1. SISTER CHROMATID EXCHANGES (SCE) IN L-2 CELLS FOLLOWING EXPOSURE TO SPENT OIL SHALE

Dose mg/ml	Chromosome Number (Mean)	Number Chromosomes Scored*	Total Number SCE	SCE Per Chromosome	SCE Per Metaphase (Mean)±
0	69	1718	209	0.12	8.4 ± 2.00
0.1	70	1813	311	0.17	12.0 ± 0.12

* 25 Metaphase spreads were analyzed at 0 dose and 26 at 0.10 mg/ml.

± Range of SCE/metaphase was from 5-13 for controls and 7-17 for the treated.

DISCUSSION

It can be concluded that under the conditions of these experiments, the spent oil shale composite affected the reproductive integrity of the cells and the ability of cells to form colonies. L-2 cells were more sensitive than CHO cells. Chromosome aberrations were produced and DNA synthesis was to a certain extent impaired in CHO cells. Mutagenicity in nude mice was not shown after treating CHO and L-2 cells with different doses of oil shale and for different lengths of time.

It is not known what material in the retorted oil shale is responsible for producing loss of some cellular function *in vitro*, but it is possible that leaching out of a metal or metals from the composite, could be responsible.

The data in this report are preliminary and the effects of spent shale on cells in culture does not imply that spent oil shale may act similarily *in vivo* over an extended period of time even though chromosome aberrations were produced in lymphocytes of peripheral human blood *in vitro*. It should be noted that spent shales may have processed specific characteristics in creating a biological effect and that the effects associated with any one type of spent shale cannot necessarily be considered as typical.

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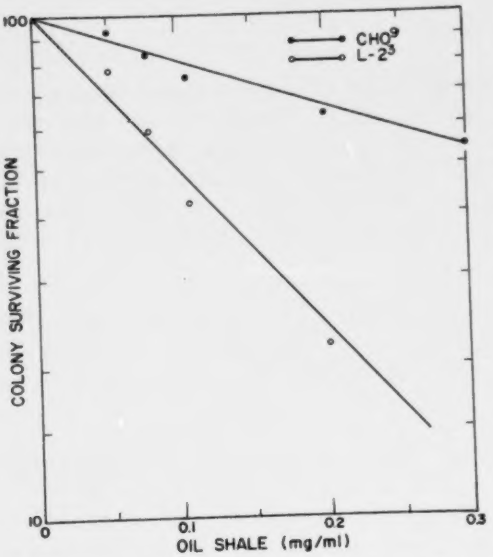

Figure 1. The survival curves for CHO and L-2 cells as measured by colony formation after exposure to oil shale. The mean lethal dose (LD_{50}) for the CHO line was 0.33 mg/ml and 0.14 mg/ml for the L-2 line.

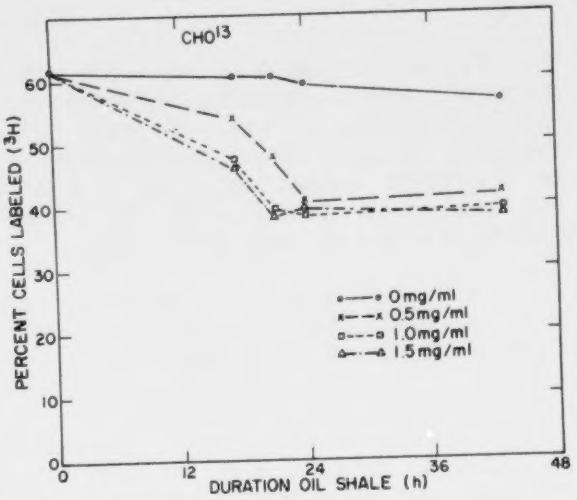

Figure 2. The percent of CHO cells labeled with tritiated thymidine [^3H] TdR as a function of the duration of oil shale following exposure to different concentrations of oil shale.

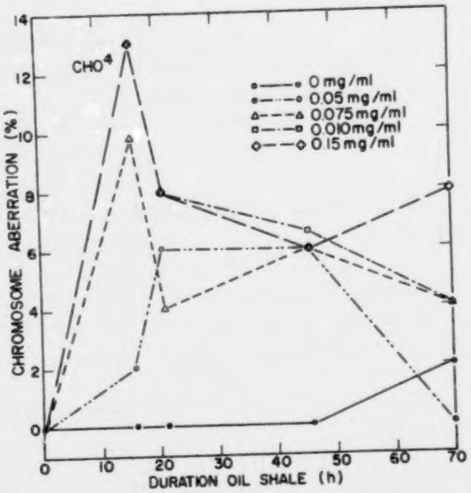

Figure 3. The frequency of chromosome aberrations in CHO cells as a function of the duration of oil shale following exposure to different concentration of oil shale.

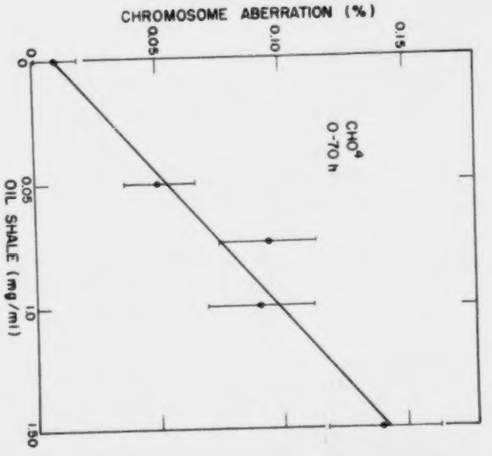

Figure 4. The accumulated frequency of chromosome aberrations in CHO cells over the 70 hour exposure period to oil shale as a function of dose.

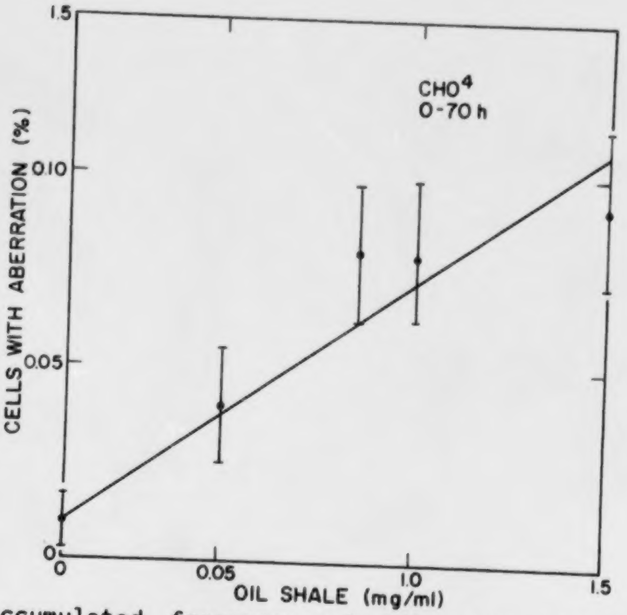

Figure 5. The accumulated frequency of CHO cells with chromosome aberrations over the 70 hour exposure period to oil shale as a function of dose.

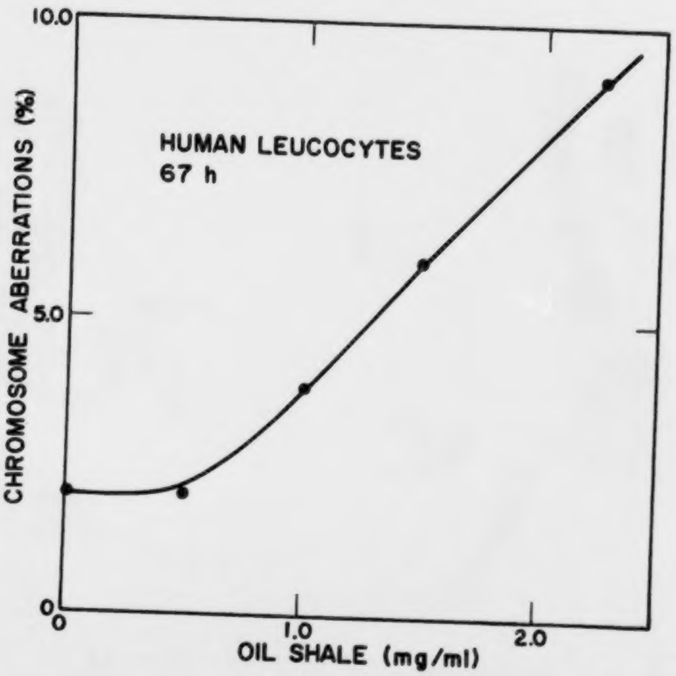

Figure 6. The frequency of chromosome aberrations in human leucocytes 67 hours after exposure to oil shale as a function of dose.

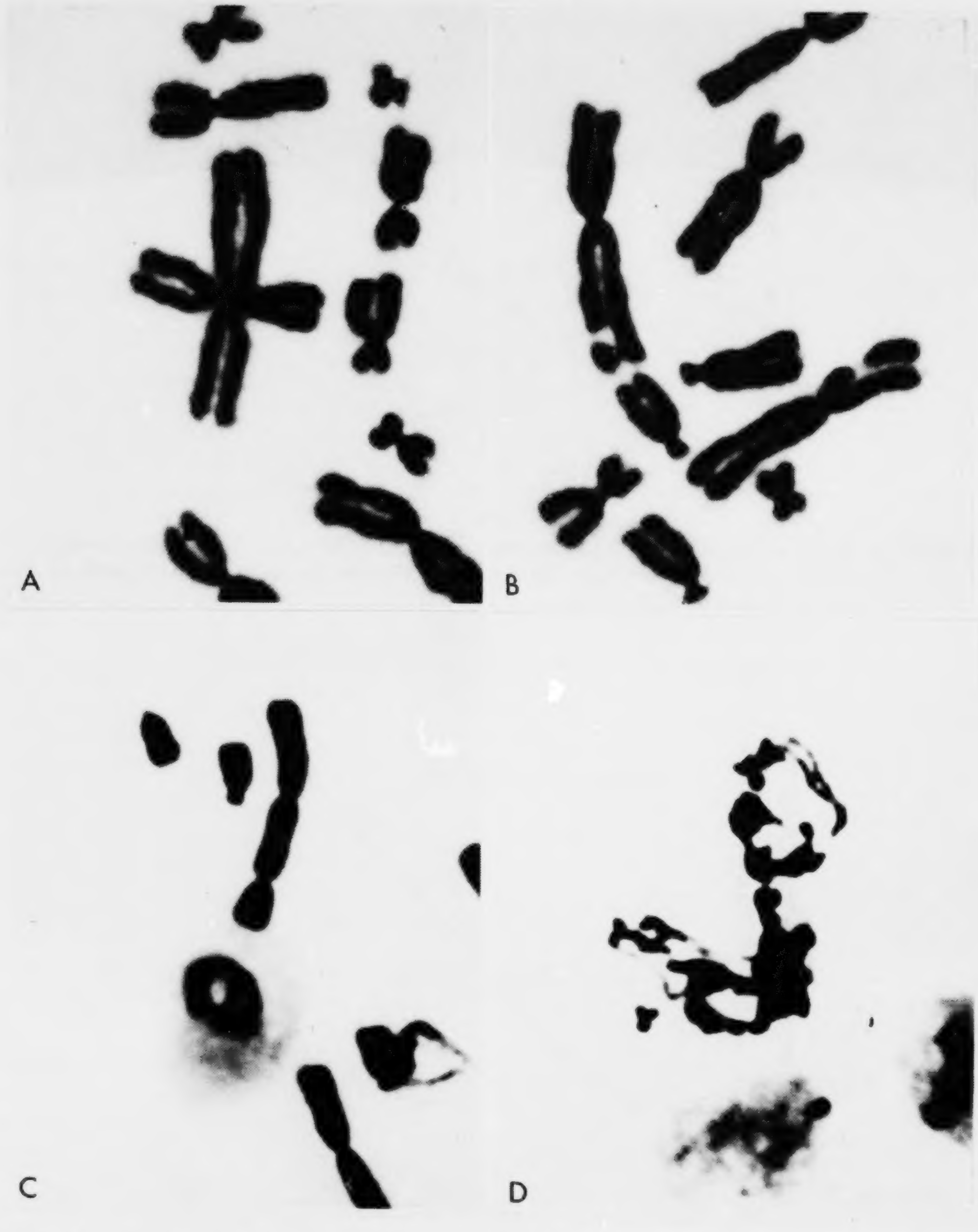

Plate 1. Types of chromosome aberrations produced in CHO cells following oil shale treatment. (a) centric fusion, (b) chromatid deletion, (c) dicentric, and (d) badly damaged chromosomes.

DETECTION OF CHEMICAL MUTAGENS IN EXTRACTS OF SPENT OIL SHALE USING THE AMES TEST

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ABSTRACT

The Ames/Salmonella-microsome test was applied to determine the carcinogenic potential of spent oil shale. Solutions of chemicals suspected to be present in extracts of spent oil shale, as well as samples of soxhlet-extracted spent shale, were assayed. Results indicate at least three different unknown chemical mutagens exist in the extracts of two spent shales. Data is also presented regarding the effect of solvent on the mutagenic response of the Ames test and the possibility that chemical interactions may mask the detection of certain mutagens in chemical mixtures.

INTRODUCTION

SPENT SHALE DISPOSAL

One of the greatest concerns regarding the operation of a full-scale oil shale industry is the environmental impact of spent shale disposal. Under natural weathering conditions, processed shale is a potential source of surface and groundwater contamination by inorganic salts, heavy metals and organic chemicals (EPA, 1971; Atwood and Coomes, 1974).

Prior to studies concerning the transport mechanisms and overall fate of these pollutants in the environment, it is essential to determine whether that activity varies with different retort processes.

CARCINOGENIC ORGANIC CHEMICALS (PAH) AND THEIR MODE OF ACTION

A component of the organic residue formed during the pyrolysis of oil shale is made up of polycyclic aromatic hydrocarbons (PAH). Selected parent compounds belonging to this class range in tumor-initiating ability from noncarcinogenic to strongly carcinogenic (Searle, 1976). It is hypothesized that there is a common mode of carcinogenic activity related to chemical structure which results in abnormal function of somatic cells (Chu, 1979; McKinney et al., 1979). When PAH compounds are metabolized (often to an epoxide form), the molecule is thought to intercalate into the DNA and form a colavent bond with that structure (Marx, 1978). This process represents a type of mutation. In the absence of DNA excision repair, replication would proceed with the mutation incorporated in the genome. If the cell remained viable, its function could be altered by the mutation.

A microbiological growth test that depends on this type of mutation could serve as a bioassay to detect chemical carcinogens which produce their effect by somatic mutation.

AMES TEST FOR MUTAGENS

The Ames test is an example of such a bioassay and the following brief description outlines the principles of the test (Ames, et al., 1975). Histidine-requiring mutant strains derived from the bacterium, Salmonella typhimurium, are used as the test organisms. These strains were selected for sensitivity and specificity in being reverted from a histidine requirement back to histidine independence by a wide variety of mutagens (Ames, et al., 1975). A metabolism component is essential to carcinogenesis by PAH in mammalian systems and it is incorporated into the microbial assay. Microsomal enzymes suitable for this purpose are obatined from a rat liver homogenate (S-9). A spontaneous rate of reversion exists for each TA strain (Table 1). Therefore, it is recommended (Ames et al., 1975) that the enhanced reversion rate can be attributed to the presence of a mutagen if it is at least twice the spontaneous rate. The data herein are reported as net revertants (Total Spontaneous).

OBJECTIVES

The objectives of this study were to (1) use the Ames test to detect chemical mutagens in extracts of spent oil shale, (2) to determine which extraction and concentration procedures for obtaining spent shale extract samples were suitable for Ames-mutagenicity testing, and (3) to determine whether the sensitivity of the Ames test is sufficient to allow identification of chemical mutagens in a sample of unknown composition.

MATERIALS AND METHODS

In the plate incorporation assay, the chemical is added directly to molten top agar (45 C) along with bacteria and liver homogenate (S-9) and then poured onto a petri dish containing agar media. Initially, chemicals are assayed over a wide concentration range both in the presence and absence of S-9, using each TA strain. A positive or questionable result can be confirmed by demonstrating a dose-response effect using a narrower range of concentrations (Ames et al., 1975). Several controls are included: bacterial cultures and S-9 are plated to check for contamination, spontaneous reversion rates are determined using the identical test procedure except the appropriate solvent is invcorporated without chemical, and assays of known mutagens are conducted as a positive control to determine whether the bacterial cultures are reverting normally.

In addition to known chemical solutions which serve as standards of mutagenic activity, extracts of two types of spent shale (here referred to

Table 1. Characteristics of the TA Strains used for Mutagen Testing

Strain	Spontaneous Revertants	Class of Mutations Detected
TA 1535	20	Base-pair substitution
TA 1537	20	Frame-shift
TA 1538	40	Frame-shift
TA 98	50	Frame-shift
TA 100	160	Base-pair substitution

Rat liver homogenate, S-9, added.

Table 2. Characteristics of Spent Shale Extract Samples
Assayed Using the Ames Test

UNKNOWN SAMPLES ASSAYED

Sample	Spent Shale	Days Extracted in Soxhlet and Solvent	Concentration Technique
D 1-B	A	1-Benzene, 1-Methanol	Roto. Evap.
D 2-B	A	4-Benzene, 4-Methanol	Roto. Evap.
D 2-B	A	4-Benzene, 4-Methanol	Kuderna Danish
D 3-B	B	3-Benzene, 5-Methanol	Roto. Evap.
D 3-B	B	3-Benzene, 5-Methanol	Kuderna Danish
D 5-B	A	3-Pentane	Kuderna Danish
D 6-A	A	Methanol	Roto. Evap.

as spent shale A and B), provided by our colleague, D.L. Maase, were assayed (Maase et al., 1979). Spent shale samples were obtained by soxhlet extraction, first with benzene and then separately with methanol. The methanol fraction was concentrated by either a rotating flash evaporator or a Kuderna Danish apparatus (Table 2). The concentrate was diluted with methanol and assayed along with a methanol control.

RESULTS

SPENT SHALE EXTRACTS

Three of the five spent shale extracts assayed showed a mutagenic response which was dependent upon metabolic activation. Figures 1 and 2 (fractions D-1B and D-2B, respectively) indicate that at least two chemical mutagens are extracted from spent shale A using the soxhlet extraction procedure. This is evident by the distinct pattern of mutagenic response exhibited and the particular TA strains which respond. This result is likely related to the length of time the spent shale was extracted with benzene and/or methanol. When extracted for one day with either solvent (D-1B), four strains showed a weak response (Figure 1, Table 3). When the shale was subjected to four days of extraction with either solvent (D-2B), only one strain, TA 100, showed an enhanced degree of mutation (Figure 2, Table 3). It also appears that the technique used to concentrate the extract sample D-2B, either by flash evaporation or Kuderna Danish evaporation, had little effect on the concentration and mutagenic activity of the chemical mutagen (Figure 2).

Table 3. Results of Spent Shale Extract Samples Assayed Using the Ames Test

		Results of Samples Tested		
Sample	Spent Shale	Days Extracted in Soxhlet & Solvent	Mutagen Strength	TA Strain Responding
D 1-B	A	1-Benzene, 1-Methanol	+	98,1537,1538,100
D 2-B	A	4-Benzene, 4-Methanol	+	100
D 3-B	B	3-Benzene, 5-Methanol	++	98,1537,1538,100
D 5-B	A	3-Pentane	-	none
D 6-A	A	3-Methanol	-	none

The chemical mutagen implicated by the mutagenic response of TA strains 98, 1538 and 1537 in extract D-3B from shale B, was apparently different from either mutagen detected in spent shale A (Figure 3, Table 3). The responding strains and the magnitude of response, in particular, suggest this tentative conclusion. The most sensitive strains were TA 1538 and TA 98 while TA 100 showed a very weak response.

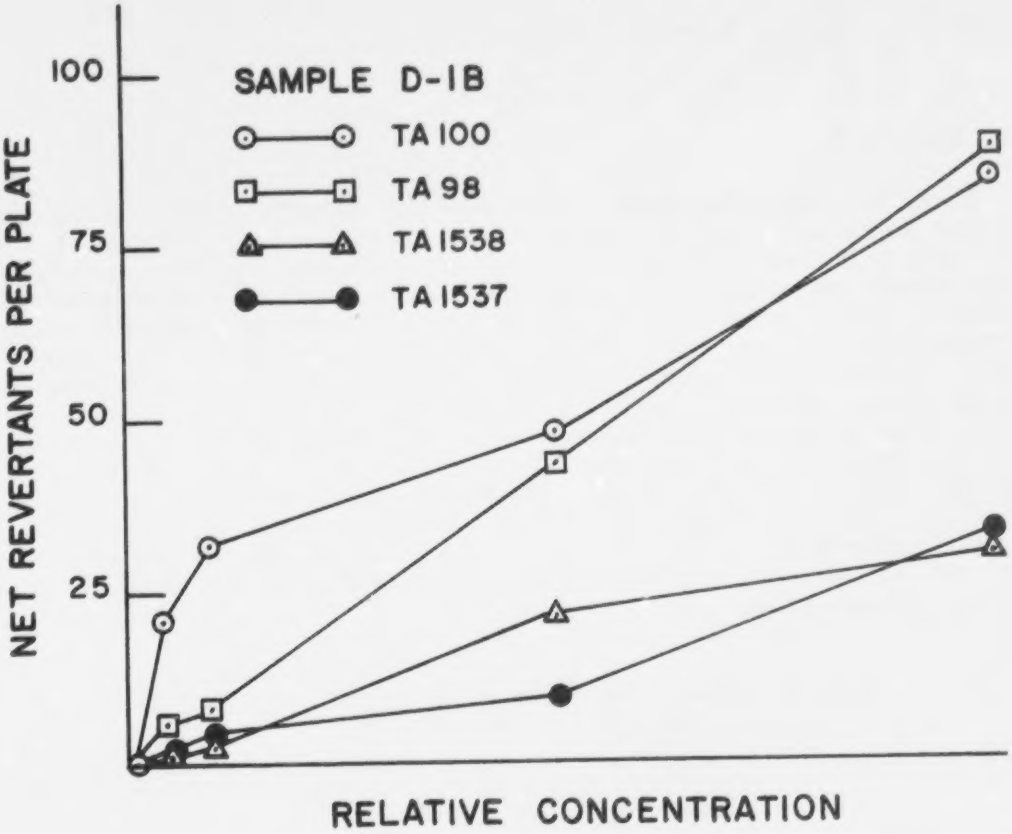

Figure 1. Mutagenic response of TA strains (98, 1537, 1538 and 100) assayed with spent shale extract sample D-1B in the presence of rat liver homogenate (S-9). Each point represents an average of four replicates. Methanol was the solvent used.

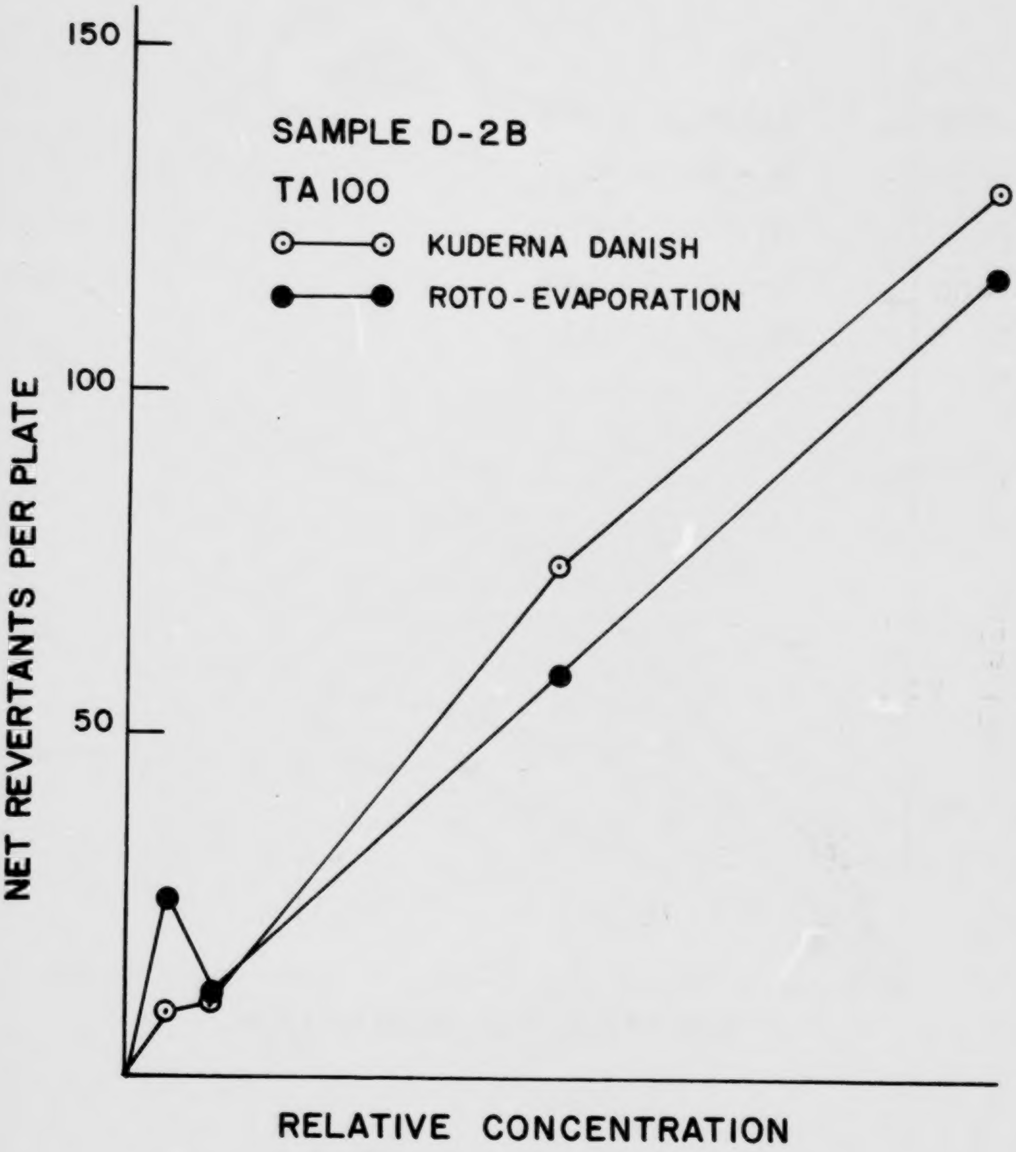

Figure 2. Mutagenic response of TA strains (100 only) assayed with spent shale extract sample D-2B in the presence of rat liver homogenate (S-9). Also shown is the effect of concentration method (Kuderna Danish or Roto-Evaporation). Each point represents an average of four replicates. Methanol was the solvent used.

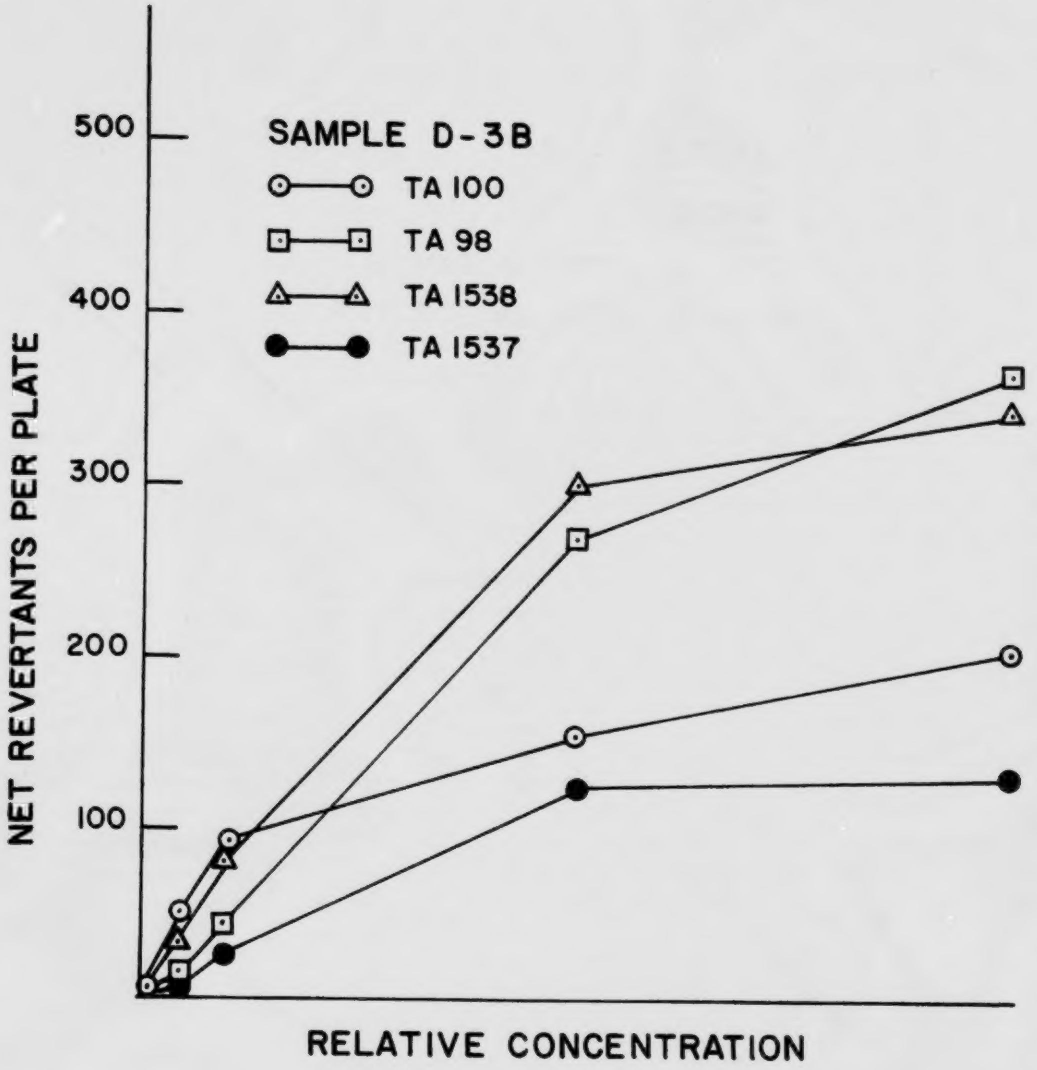

Figure 3. Mutagenic response of TA strains (98, 1538, 1537 and 100) assayed with spent shale extract sample D-3B in the presence of rat liver homogenate (S-9). Each point represents an average of four replicates. Methanol was the solvent used.

The other extracts from shale A did not yield any further information due to solvent incompatibility (pentane from extract D-5B volatilized when mixed with molten top agar) and to dilution of sample (D-6B).

KNOWN PAH COMPOUNDS

To enable identification of the unknown mutagens in the spent shale extracts, several chemicals suspected to be present were assayed using the Ames test. A unique pattern of mutagenic response, in terms of particular strains sensitive to the mutagen and the shape and magnitude of the dose-related response curves, was demonstrated for each chemical mutagen. Examples of these characteristic patterns are shown in Figures 4 and 5 for mutagens 7, 12 dimethylbenz(a)anthracene and benz(a)anthracene, respectively. The responding strains, the relative mutagenic strength of the chemical and the dose at which maximum response was detected, indicated that the characteristic pattern of mutagenic response could be used to identify chemical mutagens in a mixture of unknown composition (Table 4). For example, the presence of benzo(ghi)perylene would be indicated by the moderate response of TA 1537 at dilute concentration and no response by the other four strains.

The original testing of known chemicals was performed using dimethyl sulfoxide as the solvent. It was assumed that as long as the chemical dissolved in that solvent and the solvent was not toxic to the bacteria, that the solvent effect of mutagenic response would be negligible. However, since the unknown chemical solutions were dissolved in methanol we felt it was preferable to assay all chemical standards that were soluble in methanol in that solvent. Unfortunately, of the seven mutagens listed in Table 4, only three were soluble in methanol at a sufficiently high concentration to eliminate procedural problems (e.g., solvent toxicity). Figures 6, 7 and 8 show the comparative mutagenic response for 7, 12 dimethylbenz(a)anthracene, benz(a)anthracene and fluoranthene, respectively, in the two solvents, dimethyl sulfoxide and methanol. These figures suggest that the effect of the solvent of mutagenic response can be significant and may result in chemical toxicity.

CHEMICAL INTERACTIONS IN MIXED SOLUTIONS

Assays were conducted employing a single strain which responded uniquely to two different chemicals to determine whether the Ames test could be used to detect mutagens in chemical mixtures. These pairs included: (1) a nonmutagen with a moderate mutagen and (2) a weak mutagen and a strong mutagen. It was hypothesized that in a chemical mixture (vary concentration but same 1:1 ratio) the mutagenic response to the two mutagens would be additive. In other words the nonmutagen would antagonize the response of the moderate mutagen and the weak mutagen would enhance the response of the strong mutagen.

The results of these assays tentatively indicate that for selected chemicals a dominance hierarchy exists. In particular, the dominant chemical, benz(a)pyrene (nonmutagen for strain TA 1537) suppressed the response of TA 1537 to perylene (a strong mutagen) in a mixture (Figure 9).

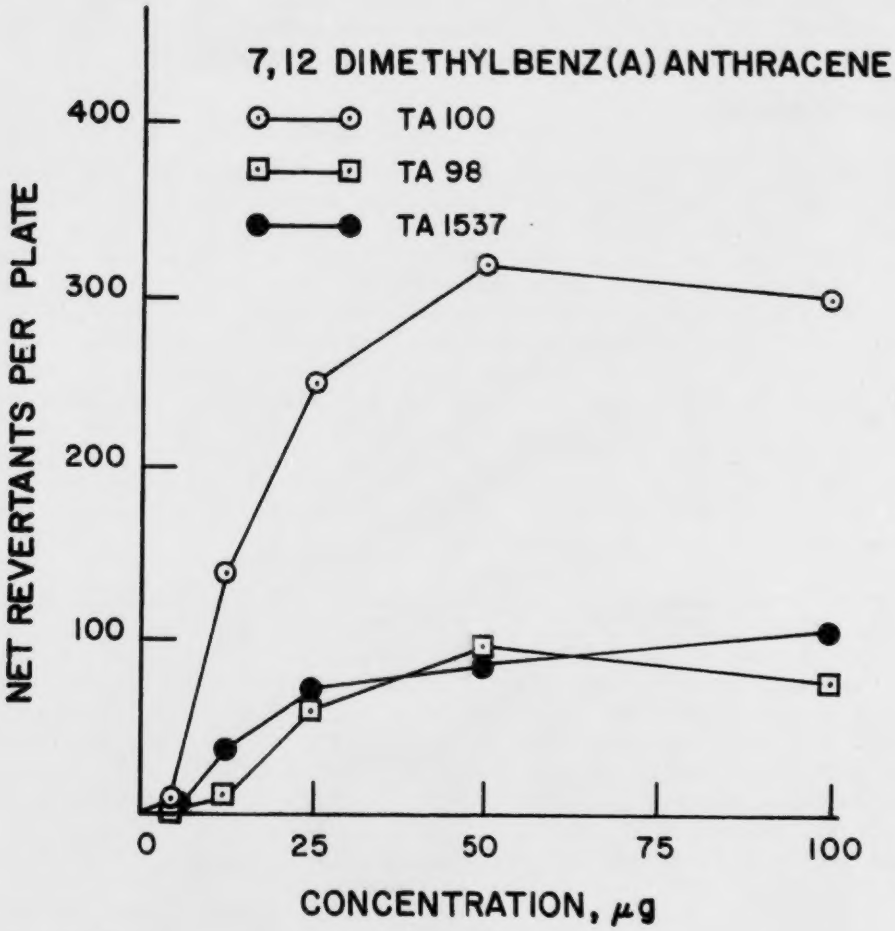

Figure 4. Mutagenic response of TA strains (100, 98 and 1537) to 7, 12 dimethylbenz(a)anthracene assayed at various concentrations in the presence of rat liver homogenate (S-9). Each point represents an average of four replicates. Methanol was the solvent used.

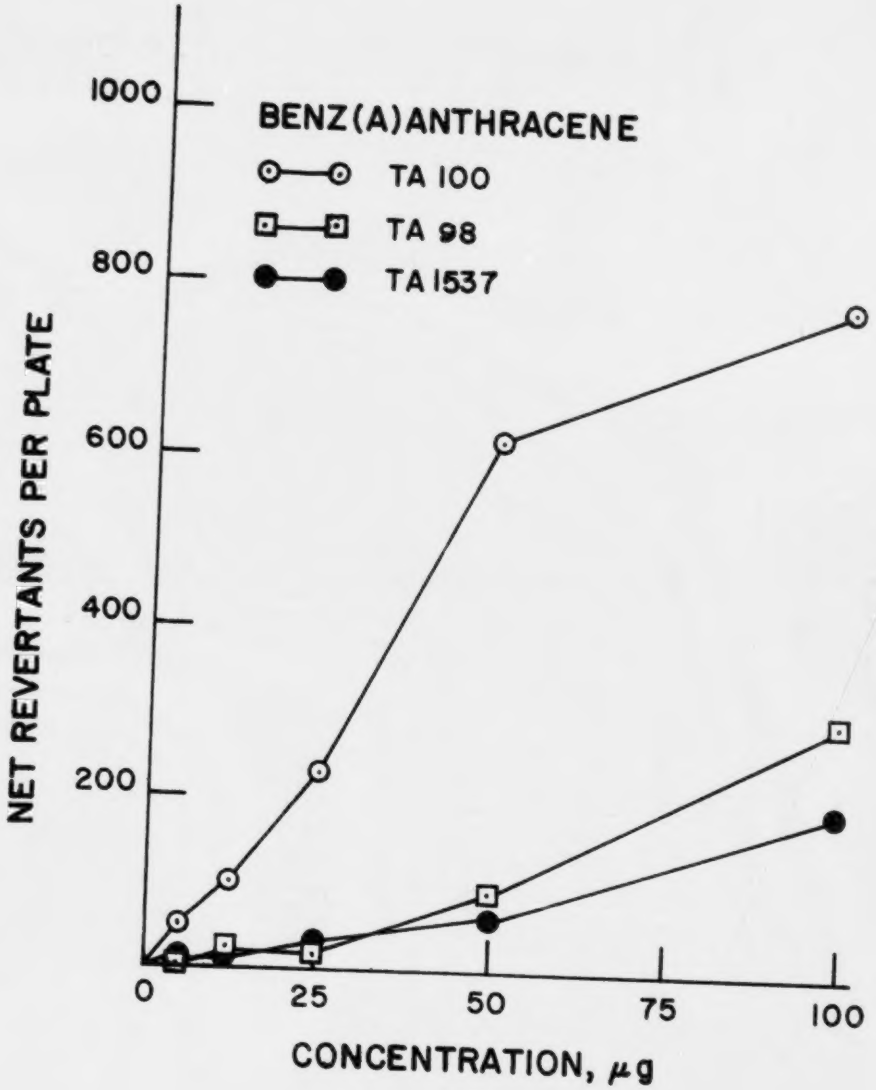

Figure 5. Mutagenic response of TA strains (100, 98 and 1537) to benz(a)anthracene assayed at various concentrations in the presence of rat liver homogenate (S-9). Each point represents an average of four replicates. Methanol was the solvent used.

Table 4. Results of known chemicals assayed using the Ames test.

RESULTS OF CHEMICALS TESTED

Compound	Strength of Mutagen	Solvent		TA Strains Responding	Concentration for Mutagenic Response
		Methanol	DMSO		
7, 12 Dimethylbenz-(a)anthracene	++	X	X	100,98,1537 1538	>25 μg/plate
Benzo(a)pyrene	+++		X	100,98,1537	5 μg/plate
Dibenz(a,h)anthracene	+		X	100,1537	25 μg/plate
Benzo(ghi)perylene	++		X	1537	>2 μg/plate
Benz(a)anthracene	+	X	X	100,98,1537	>25 μg/plate
Anthracene	–		X	none	
Phenanthrene	–		X	none	
Pyrene	–		X	none	
Perylene	+++		X	1537,98	5 μg/plate
Carbazole	–		X	none	
Fluoranthene	+	X	X	100,98	10 μg/plate

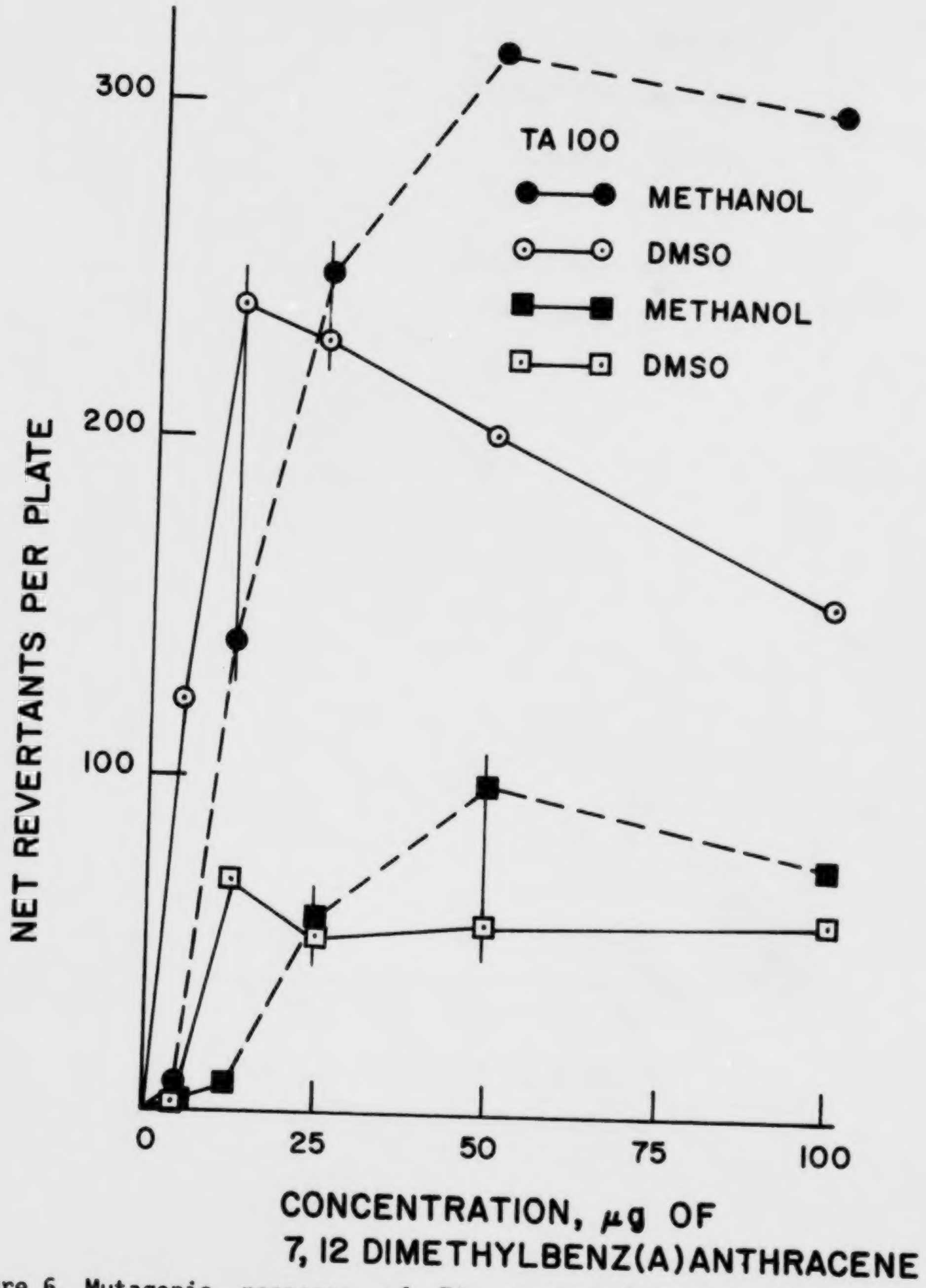

Figure 6. Mutagenic response of TA strains (100 and 98) to 7,12 dimethylbenz(a)anthracene dissolved in two solvents (dimethyl sulfoxide and methanol) in the presence of rat liver homogenate (S-9). Each point represents an average of four replicates. Thin vertical lines connecting symbols indicate values which are not statistically different (t-test, $\alpha = 0.05$).

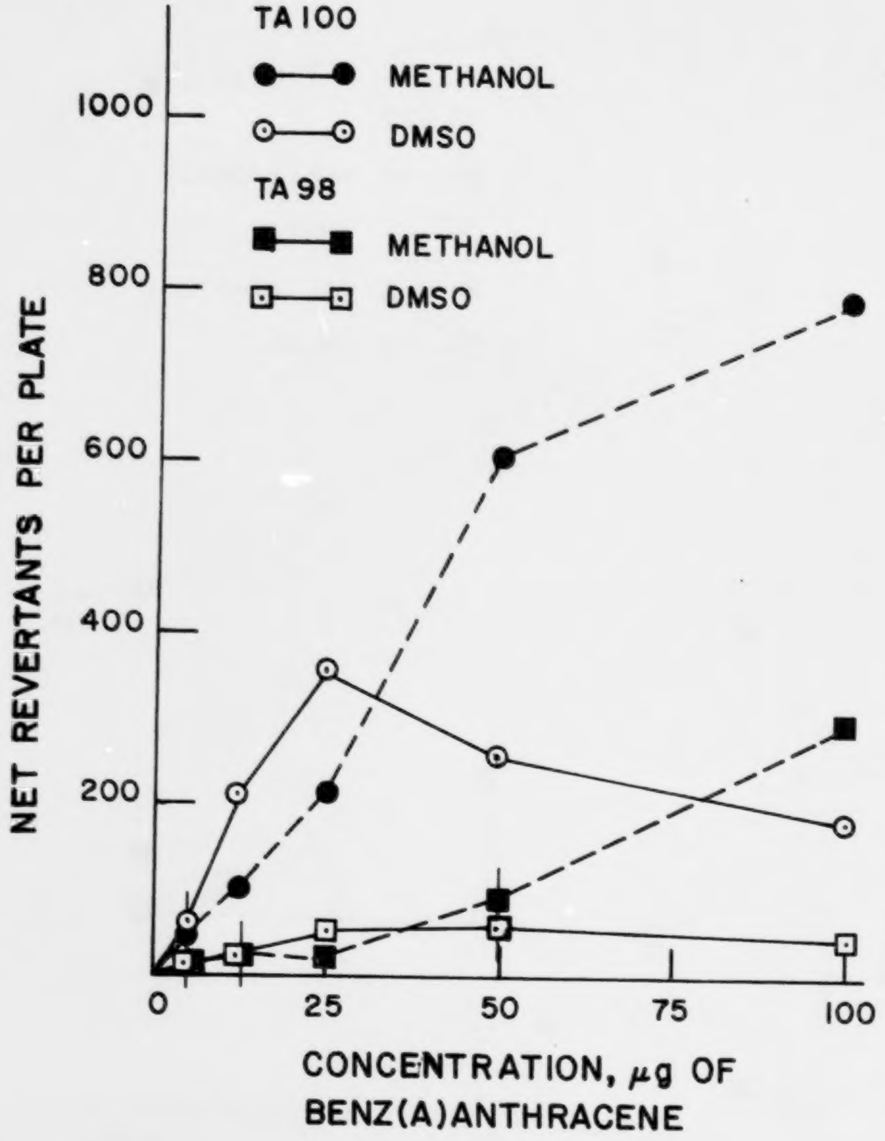

Figure 7. Mutagenic response of TA strains (100 and 98) to benz(a)-anthracene dissolved in two solvents (dimethyl sulfoxide and methanol) in the presence of rat liver homogenate (S-9). Each point represents an average of four replicates. This vertical lines connecting symbols indicate values which are not statistically different (t-test, $\alpha = 0.05$).

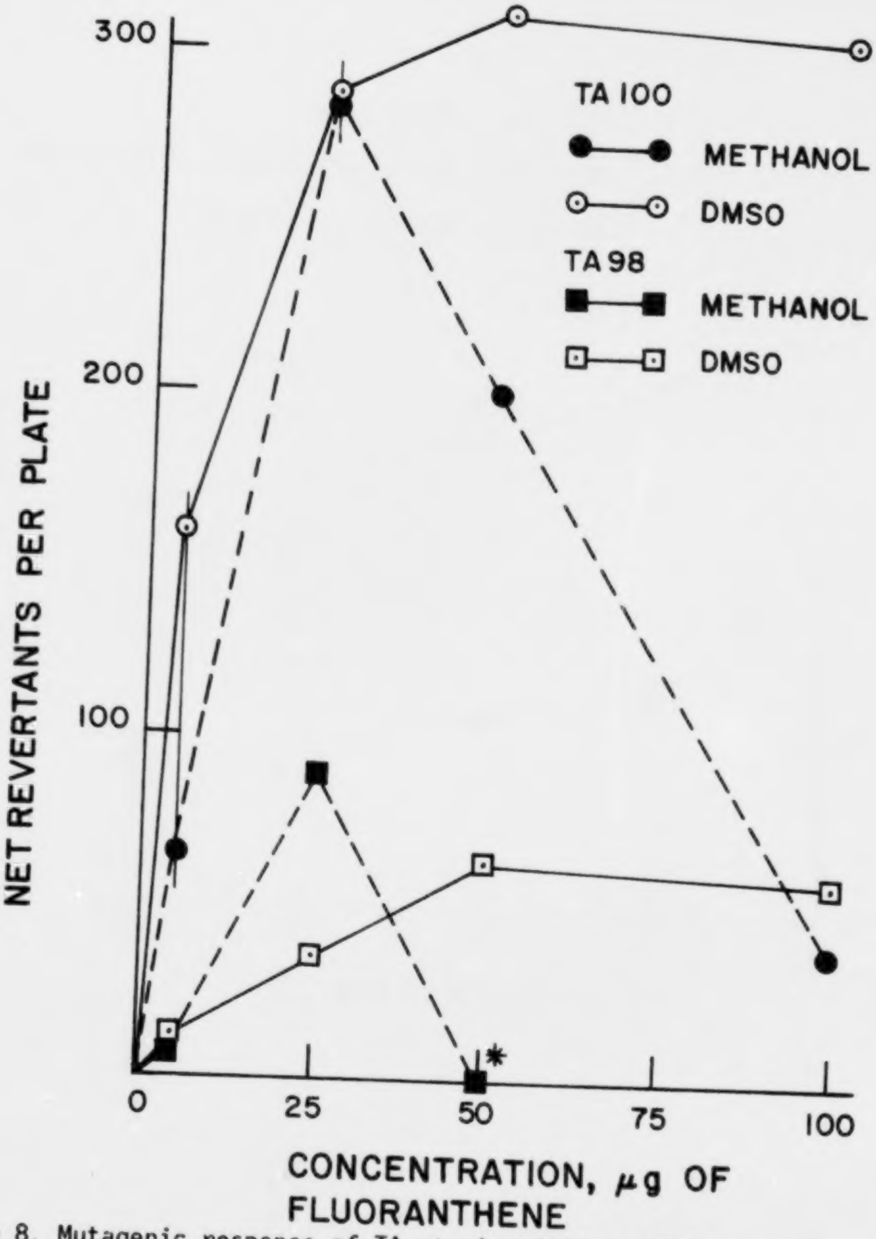

Figure 8. Mutagenic response of TA strains (100 and 98) to fluoranthene dissolved in two solvents (dimethyl sulfoxide and methanol) in the presence of rat liver homogenate (S-9). Each point represents an average of four replicates. Thin vertical lines connecting symbols indicate values which are not statistically different (t-test, $\alpha = 0.05$). * indicates that the mutagenic response of strain 98 for concentrations >50 μg was less than the spontaneous reversion value resulting in a negative number for net revertants per plate.

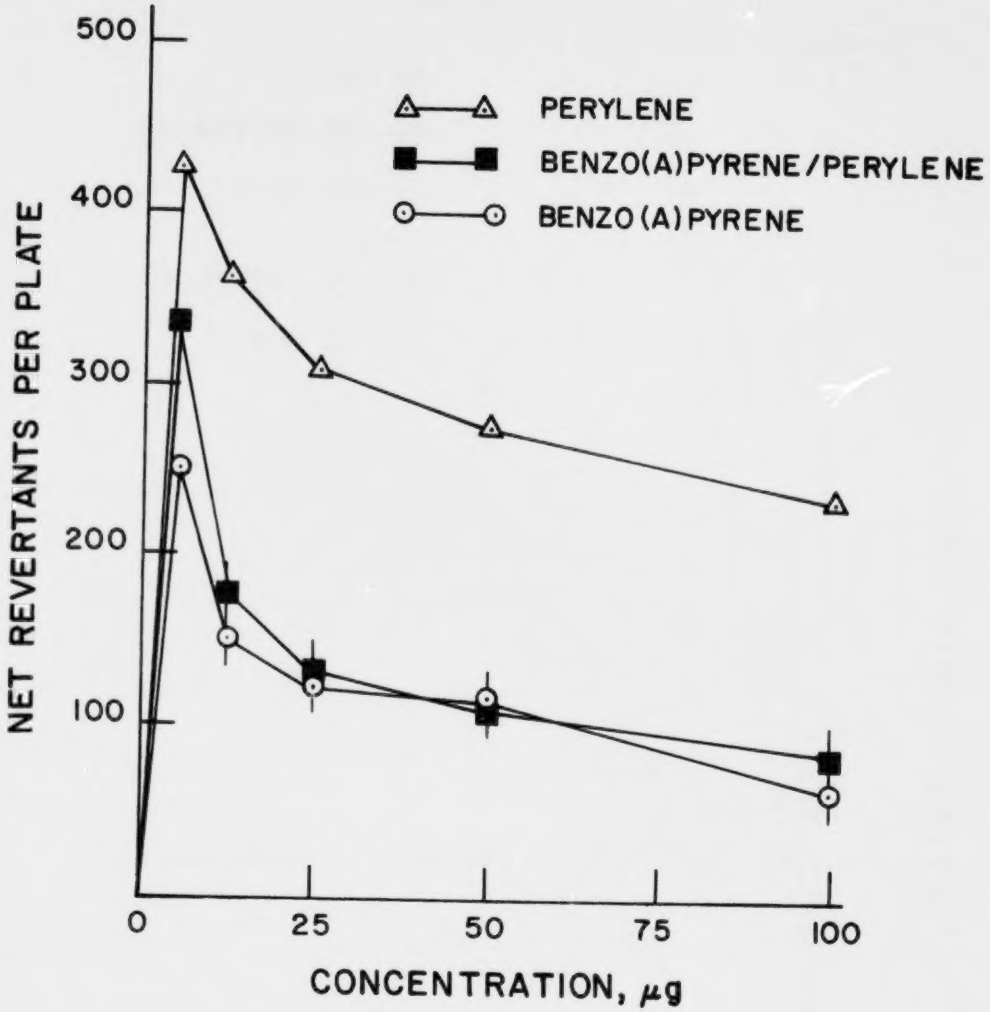

Figure 9. Mutagenic response of TA 1537 to chemicals perylene and benzo(a)pyrene assayed separately and together in a chemical mixture (1:1 ratio, by weight) in the presence of rat liver homogenate (S-9). Each point represents an average of four replicates. Dimethyl sulfoxide was the solvent used. Thin vertical lines connecting symbols indicate values which are not statistically different (t-test, $\alpha = 0.05$).

Alternatively, the presence of 7, 12 dimethylbenz(a)anthracene was not detected when it was assayed along with benzo(a)pyrene (a strong mutagen) using TA 98 (Figure 10).

With most chemical pairs assayed in a 1:1 solution, the dominance seemed to be complete; the mutagenic response to the mixture could not be distinguished from the mutagenic response to one of the chemicals alone. These data suggest that the presence of certain chemicals can mask the detection of subordinant mutagens in the Ames test. For this reason, samples of unknown composition should be fractionated prior to mutagenic testing.

DISCUSSION

While three apparently different chemical mutagens were detected in extracts of spent oil shale using the Ames test, unanticipated problems of solvent effect on mutagenicity and chemical insolubility limited the number of known chemical mutagen standards that could be used for identification purposes. For these reasons it is nearly impossible to attempt identification based either on the results presented herein or reported elsewhere.

The Ames test proved successful in detecting potential environmental carcinogens in spent shale extracts. The nature of chemical interactions shown to exist in solutions cannot preclude the possibility that other mutagens are present in these mixtures or that samples not showing mutagenic activity are without mutagens. We agree that the Ames test is a powerful tool for use in the detection of environmental carcinogens, however, we emphasize that it should be used as originally intended, for initial screening and should be followed by other testing procedures.

CONCLUSIONS

Regarding the objectives of this study, the following conclusions were made:

1. The Ames test has been found suitable for the detection of chemical mutagens in refined extracts of spent oil shale.
2. The soxhlet procedure using a combination of solvents, benzene and methanol, has been found effective in isolating chemical mutagens from spent oil shale.
3. Although pentane is an effective extraction solvent, the solution should be prepared by evaporating and redissolving in another more suitable solvent (dimethyl sulfoxide or methanol) prior to mutagenicity testing.
4. Use of the Ames test for identification of chemical mutagens in a sample of unknown composition appears limited at this time, due to the effect of solvent on mutagenic response and the lack of knowledge regarding the nature of chemical interactions in mixed solutions.

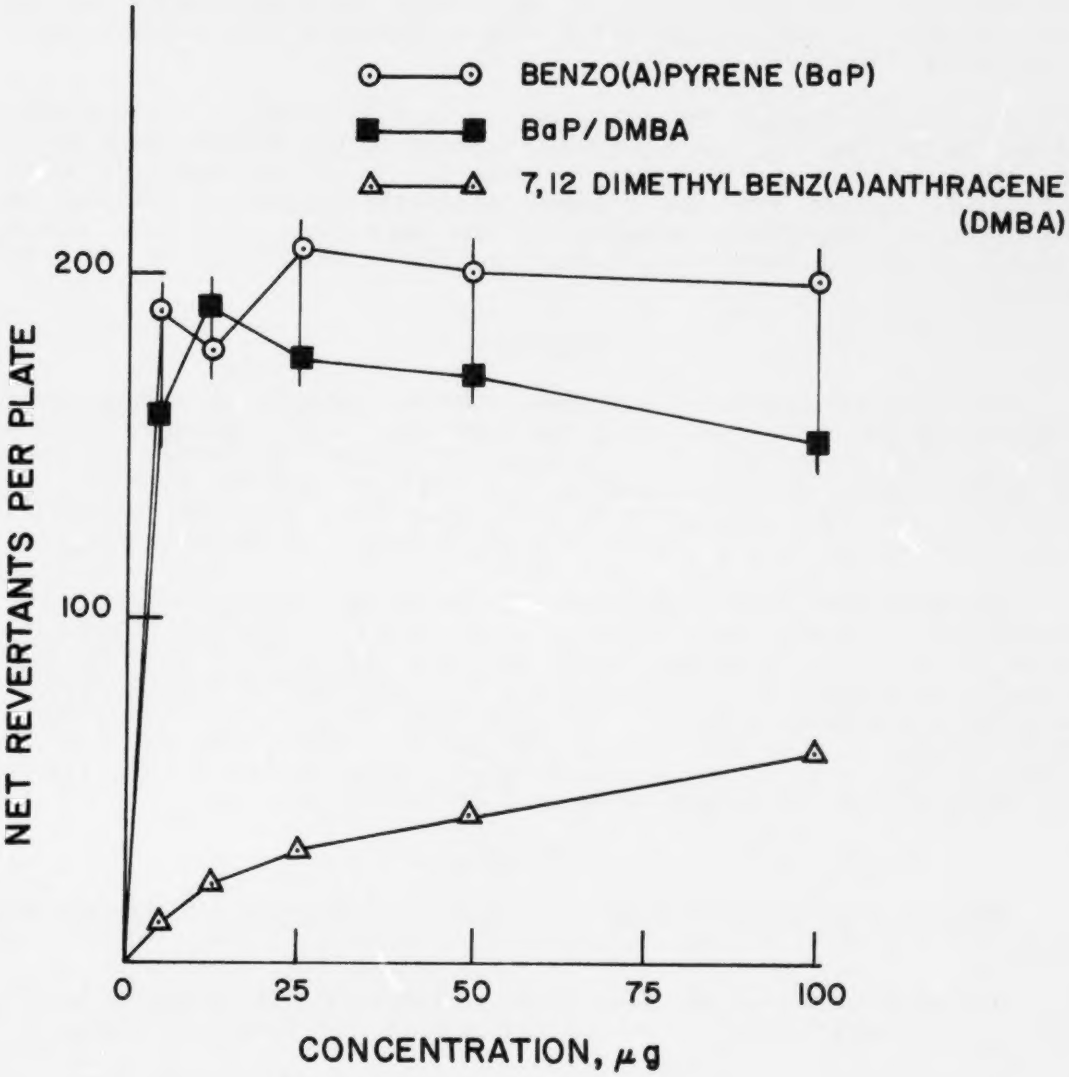

Figure 10. Mutagenic response of TA 98 to chemicals benzo(a)pyrene and 7,12 dimethylbenz(a)anthracene assayed separately and together in a chemical mixture (1:1 ratio, by weight) in the presence of rat liver homogenate (S-9). Each point represents an average of four replicates. Dimethyl sulfoxide was the solvent used. Thin vertical lines connecting symbols indicate values which are not statistically different (t-test, $\alpha = 0.05$).

ACKNOWLEDGEMENTS

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FLOW CYTOMETRIC METHODS FOR ASSAYING DAMAGE TO RESPIRATORY TRACT CELLS

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ABSTRACT

This paper summarizes results of experiments designed to develop automated flow-analysis assay methods for discerning damage to exfoliated respiratory tract cells in model test animals exposed by inhalation to physical and chemical agents associated with the production of synthetic fuels from oil shale, the specific goal being the determination of atypical changes in exposed lung macrophages and epithelial cells. Animals were exposed to oil shale particulates (raw and spent), silica, and ozone, and respiratory tract cells were obtained by lavaging the lungs with normal saline. Cell samples were stained with fluorescent dyes specific for different biochemical parameters and analyzed as they flowed through a chamber intersecting a laser beam(s) of exciting light where sensors measured fluorescence and light scatter (cell size) on a cell-by-cell basis. Cellular parameters proportional to optical signals were displayed as frequency distribution histograms. Cells also were separated according to cytological features and identified. The basic features of the methodology are presented, along with examples of results that illustrate characterization and analysis of normal and exposed respiratory tract cells based on DNA content, total protein, size, and phagocytic activity.

INTRODUCTION

The application of advanced flow cytometric instrumentation to measure cytological and biochemical properties of respiratory tract cells provides a new approach for assessing potential damage to lung epithelium exposed by inhalation to toxic environmental pollutants associated with the production of synthetic fuels from oil shale and coal.[1-5] This includes development of automated cytological methods for determining atypical changes in exfoliated respiratory tract cells from experimental animals, the end objective being examination of sputum samples from exposed humans. To develop analytical flow-analysis methods for quantitative assessment of cellular damage, automated cell-analysis and sorting instrumentation[6-8] is being applied to study respiratory tract cells from hamsters exposed to particulates of oil shale, silica, and ozone. This includes the acquisition of exfoliated lung cells by lavaging the respiratory tract with normal saline; utilization of fluorescence staining methods to measure cellular biochemical parameters; and exposure of experimental animals to physical and chemical toxicants, followed by flow cytometric analysis. Examples of results from initial studies involving measurement of DNA content and total protein in normal and exposed respiratory tract cells are presented, along with a brief description of the instrumentation technique. A new method for quantitating pulmonary macrophage phagocytosis in rats using fluorescent microspheres also is under development. This technology provides a new approach for studying the mechanisms of damage to respiratory tract cells, with future anticipated results serving to assist in estimating risks, evaluating dose-damage relationships, and establishing guidelines for determining exposure levels to humans.

MATERIALS AND METHODS

The principle of measurement is illustrated in Figure 1. Normal and exposed respiratory tract cells composed of macrophages, leukocytes, ciliated columnar and basal undifferentiated cells stained with fluorescent dyes were analyzed in liquid suspension as they flowed through a chamber intersecting a laser beam(s) of exciting light.[9,10] Multiple sensors measured fluorescence and light-scatter optical signals on a cell-by-cell basis. Cellular parameters proportional to optical measurement (e.g., DNA content, total protein, cell size, and phagocytic activity) were displayed as frequency distribution histograms using a multichannel pulse-height analyzer. Cells also were separated according to various cytologic parameters and identified microscopically.

To study cellular changes in animals exposed to particulates of oil shale and silica, Syrian hamsters were injected intratracheally with 10 mg of ball-milled (2- to 7-μm diameter range) raw and spent oil shale and silica (4-μm mean diameter) suspended in 0.2 ml of normal saline. Hamsters were exposed also to 0.2 ml of saline alone. Raw shale (type 2) was obtained from Anvil Points, Colorado. The two spent shales (types 1 and 2) were from solid heat transfer and gas combustion processes, respectively. Silica was obtained from the Pennsylvania Glass and Sand Corporation. Hamsters anesthetized with "Brevital" (5 mg) prior to intratracheal instillation of particulates and saline via the oral cavity were returned to the colony. Animals were sacrificed by pentobarbital injection 28, 35, and 42 days later. The lungs were then lavaged four times with saline to obtain exfoliated cells, which were fixed in 35% ethanol prior to staining for DNA content with mithramycin,[11,12] excited at 457 nm wavelength (argon laser), and analyzed for fluorescence properties.

Syrian hamsters also were exposed to acute levels of ozone (4 ppm for 4 hour) and sacrificed at different times ranging from 0 to 56 hour after termination of exposure. Respiratory tract cells were obtained at sacrifice using pentobarbital, followed by lavaging the lungs with saline, fixing in ethanol, staining with mithramycin (DNA content), and analysis.

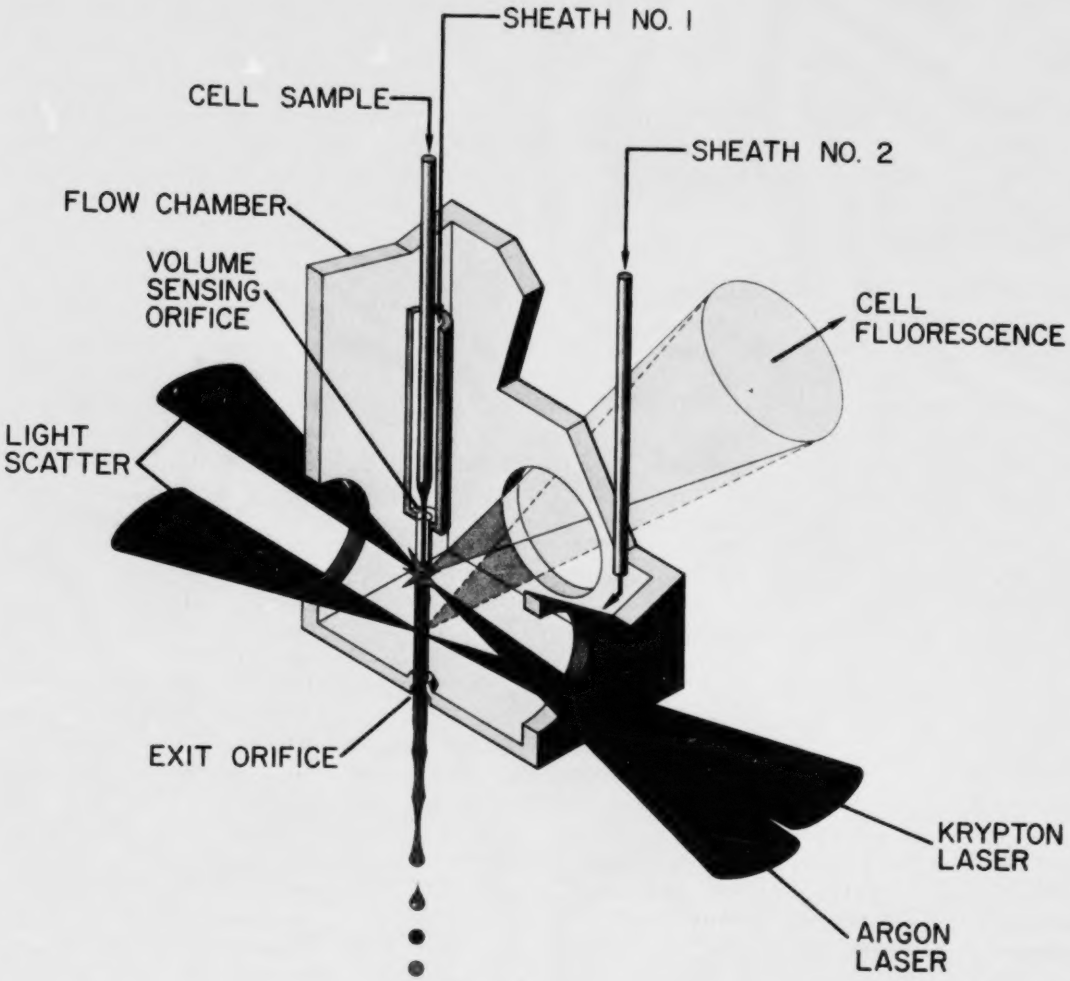

Figure 1. Cutaway view of the multiparameter cell separator flow chamber, illustrating dual-laser excitation.

Normal hamster respiratory tract cells also were characterized initially based on DNA content and total protein. Cells were obtained by sacrifice, followed by lung lavage using saline. DNA content and total protein were measured by fixing the cells in 35% ethanol, staining with mithramycin (DNA) and rhodamine 640 (protein), and analyzed for two-color fluorescence properties by exciting bound fluorochromes at 457 nm (argon laser) and 468 nm (krypton laser), respectively.[10]

To develop an automated method for quantitating alveolar macrophage phagocytosis, normal Sprague-Dawley rats were anesthetized by inhalation of Metafane. The trachea was then intubated with a blunt needle via the oral cavity, and 1 to 2 x 10^7 polystyrene latex spheres (fluorescent) of 1.83-μm diameter suspended in 0.5 ml of saline were delivered to the respiratory tract. After 2 hours, rats were sacrificed by pentobarbital injection and their lungs lavaged with 4 ml of saline (four times). Cells were fixed in 35% ethanol, rinsed and resuspended in saline, excited at 457 nm (argon laser), and analyzed for fluorescence (phagocytized spheres) and light scatter (size).

RESULTS AND DISCUSSION

DNA Measurements: Respiratory Tract Cells Exposed to Oil Shale Particulates and Silica

To initiate studies with classes of particulates and known toxic agents, hamsters were exposed to raw and spent oil shale particulates and silica by intratracheal injection. Since DNA content distributions showed no significant changes compared to controls up to 28 days after exposure, it was decided to examine respiratory tract cells that had been exposed 28 days or more. Figure 2 shows the DNA content per cell distribution of respiratory tract cells from hamsters exposed to saline, silica, and raw and spent oil shale particulates 28, 35, and 42 days after exposure. DNA content distributions of normal control animals are shown in Figure. 2A. Peak 1 represents cells having 2C DNA content and peak 2 binucleated cells and doublets (4C DNA content).[5] DNA content distributions of lung cells from hamsters exposed to saline (Figure. 2B) closely resemble controls. However, DNA content distributions of lung cells from hamsters exposed to silica (Figure. 2C), which appear normal at 28 days postexposure, begin to show atypical changes at 35 and 42 days. A third region has appeared to the left of peak 1, which is most likely dead cells. At 42 days, cells within region 3 have increased and a shoulder is beginning to develop on the right side of peak 1. The percentage of binucleated cells appears to be increasing also. Preliminary DNA content distributions of lung cells exposed to raw and spent oil shale are shown in Figs. 2D, 2E, and 2F. Figure 2D illustrates DNA content distributions of lung cells exposed to type 1 spent shale. These distributions appear nearly normal, with the exception that the left side of peak 1 is skewed.

DNA content distributions from respiratory tract cells exposed to type 2 raw and spent shale are shown in Figs. 2E and 2F, respectively. Distributions from hamsters exposed to raw shale appear nearly normal;

however, DNA content distributions from hamsters exposed to spent shale show atypical changes 35 and 42 days postinstillation. A definite shoulder appeared on the right side of peak 1, and the number of cells within region 3 increased. These changes were better observed by increasing the amplifier gain of the fluorescence channel, thus centering peak 1 in channel 30 of the multichannel pulse-height analyzer (Figure. 3). Peak 1 now shows a well-defined region of cells to the right side that is similar to the results from hamsters exposed to ozone, as described below. Although these cells have not been identified at this time, experiments are under way to determine the cell types present in peaks 1 and 3.

DNA Measurements: Respiratory Tract Cells Exposed to Ozone

Hamsters were exposed to acute levels of ozone (4 ppm for 4 hour) and sacrificed at different times after exposure. These results are shown in Figure. 4. Figure 4A shows a typical DNA content distribution obtained on a normal (control) hamster. DNA content distributions obtained from a hamster immediately at (0 hour) and 1 hour after exposure are shown in Figs. 4B and 4C. Peaks 1 and 2 both show a general broadening, with an increase in the total number of cells contained in peak 2 (binucleated cells and doublets). DNA content distributions measured on hamster lung cells 3, 5, and 7 hour after exposure (Figs. 4D, 4E, and 4F) appear similar. Peak 1 is divided into two separate parts (bimodal distribution), whereas the number of cells contained within peak 2 has diminished. The DNA distribution of hamster respiratory tract cells 28 hour after exposure is shown in Figure. 4G. This distribution, which is similar to those recorded in Figs. 4D, 4E, and 4F, has an increased percentage of cells between peaks 1 and 2. Figure 4H shows a DNA content distribution for hamster cells 48 hour after exposure, which "resembles" a typical DNA distribution for randomly growing CHO cells in which peak 1 represents G_1-phase cells (2C DNA content) and peak 2 G_2 and M-phase cells (4C DNA content). Cells located between peaks 1 and 2 would then be S-phase cells. In Figure. 4I (56 hour after exposure), the DNA content distribution per cell has reverted back to resemble distributions recorded at earlier times after exposure (Figs. 4D, 4E, and 4F).

These initial results vividly demonstrate the importance of using flow cytometric analysis methods as a new methodology to study the effects of exposure and recovery to known toxic agents. Future experiments will consist of verifying these results, studying other time increments after exposure, and correlating cytology (morphological features, differential cell counts, etc.) with DNA content measurements. Cells also will be sorted and microscopically identified. DNA measurements also can be used to study cell-cycle kinetics and would thus permit recovery mechanisms to be analyzed dynamically, especially when coupled with other cellular parameters (e.g., protein, enzymes, etc.) using multiparameter analysis methods.

DNA-Protein Measurements: Normal Respiratory Tract Cells

A new dual-laser multiparameter flow system has broad potential application in basic cell biology research, including the analysis of respiratory tract cells. This system has been used recently to measure DNA content with

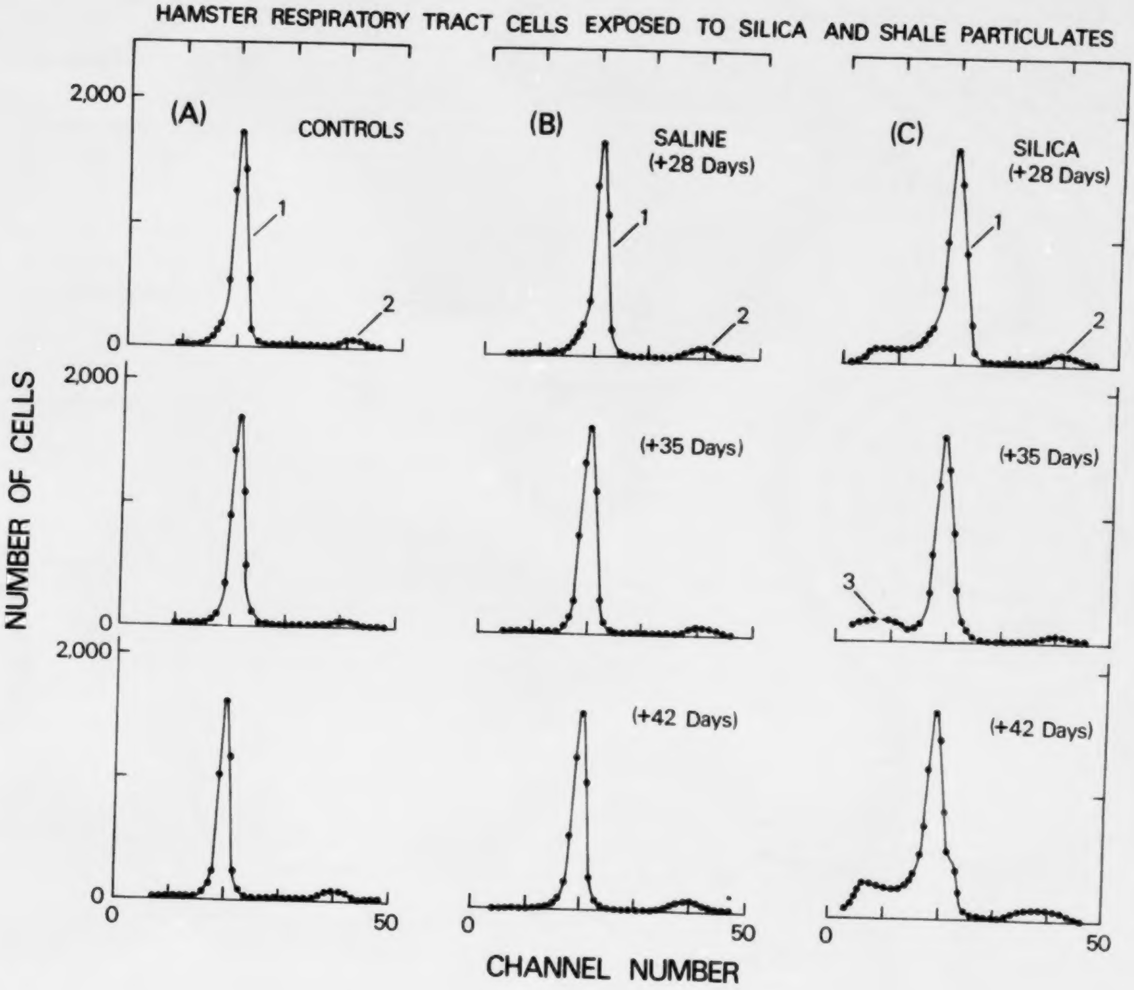

Figure 2. (2A, 2B, and 2C). The DNA content per cell distribution of respiratory tract cells from hamsters under control, saline and silica exposures.

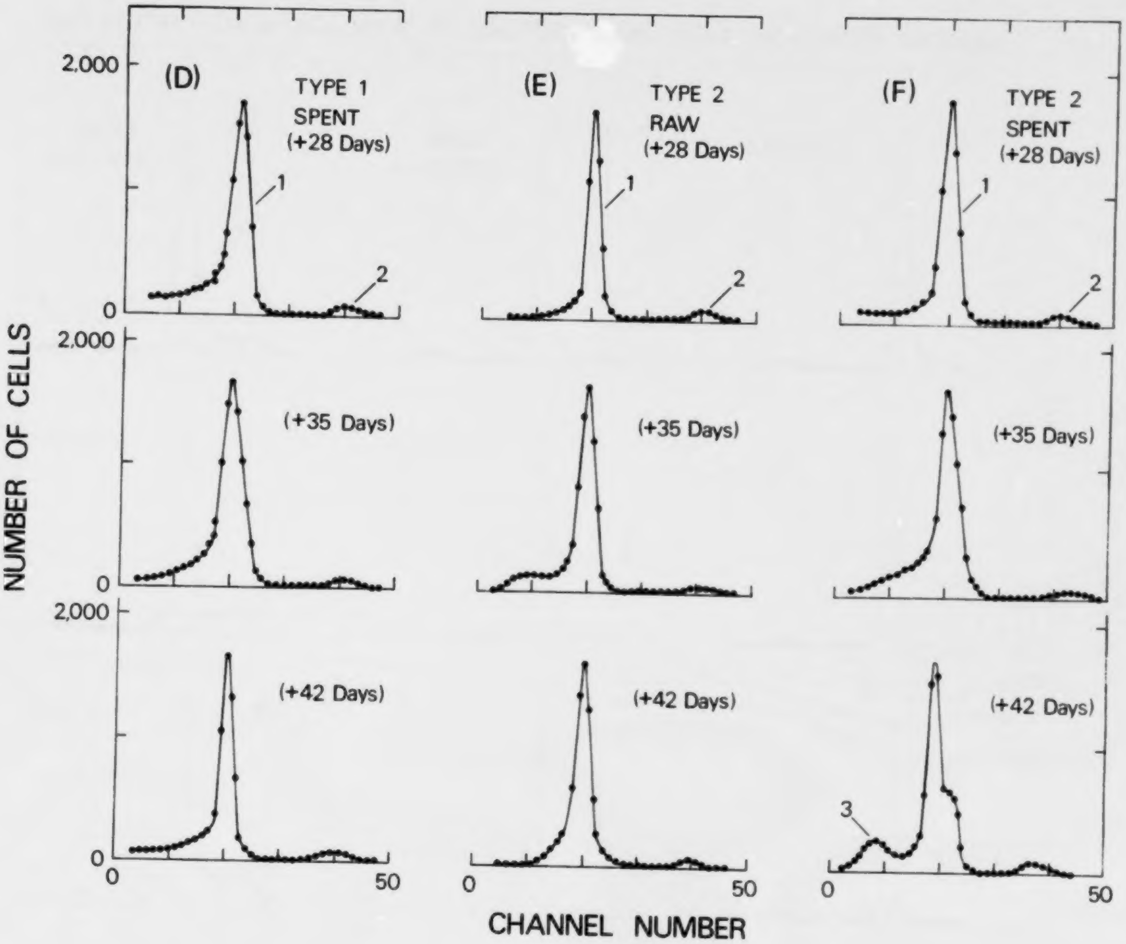

Figure 2. (2D, 2E, and 2F). DNA content frequency distribution histograms of hamster respiratory tract cells exposed (intratracheal injection) to type 1 spent shale, and type 2 raw and spent shale prior to sacrificing 28, 35, and 42 days later. Cell samples were obtained by lung lavage, fixed in 35% ethanol, stained with mithramycin, and analyzed for fluorescence. Types 1 and 2 spent shales were obtained from solid heat transfer and gas combustion processes, respectively.

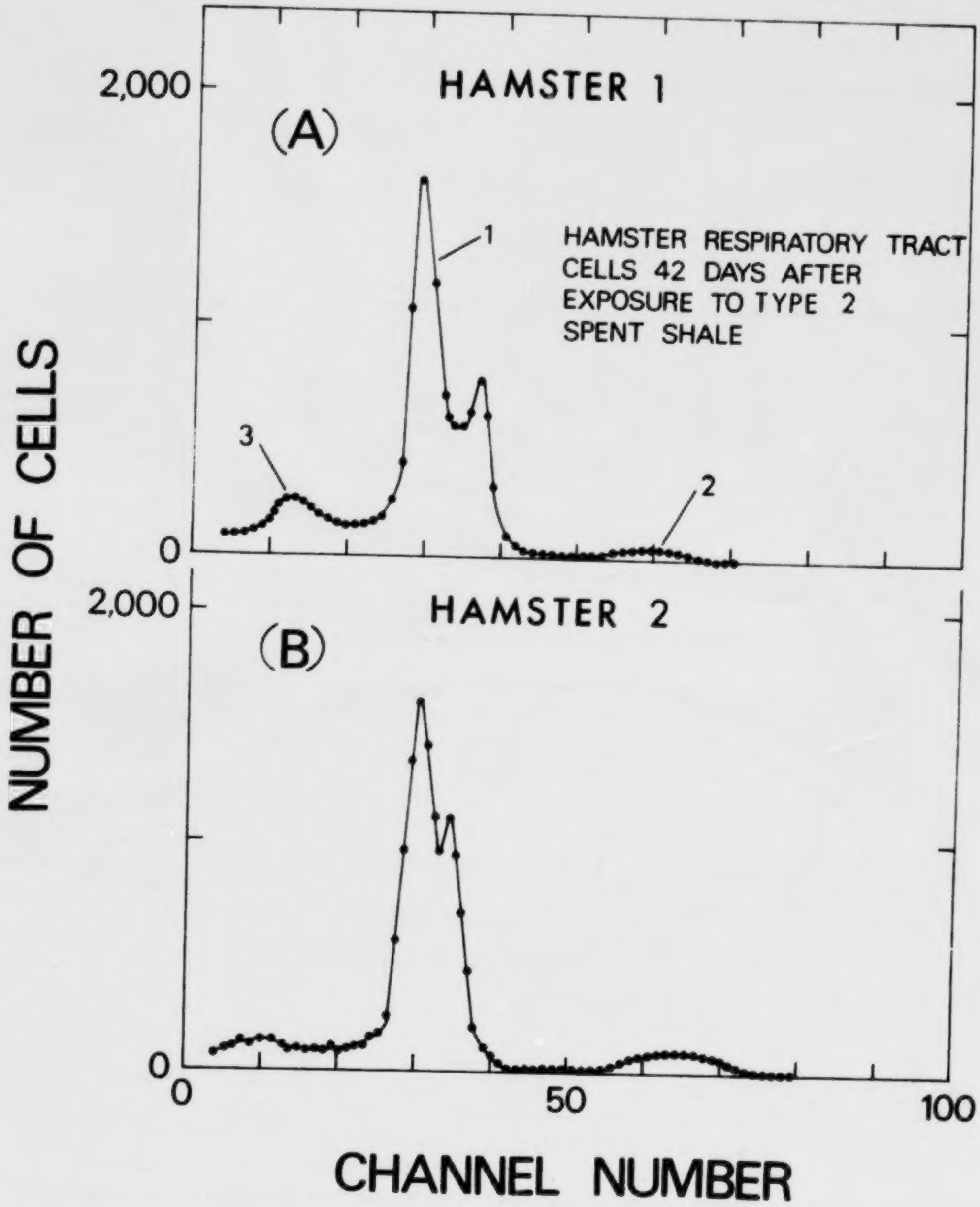

Figure 3. DNA content frequency distribution histrograms of hamster respiratory tract cells exposed (intratracheal injection) to type 2 spent shale prior to sacrificing 42 days later. Cell samples were obtained by lung lavage, fixed in 35% ethanol, stained with mithramycin, and analyzed for fluorescence. Type 2 spent shale was obtained from a gas combustion process.

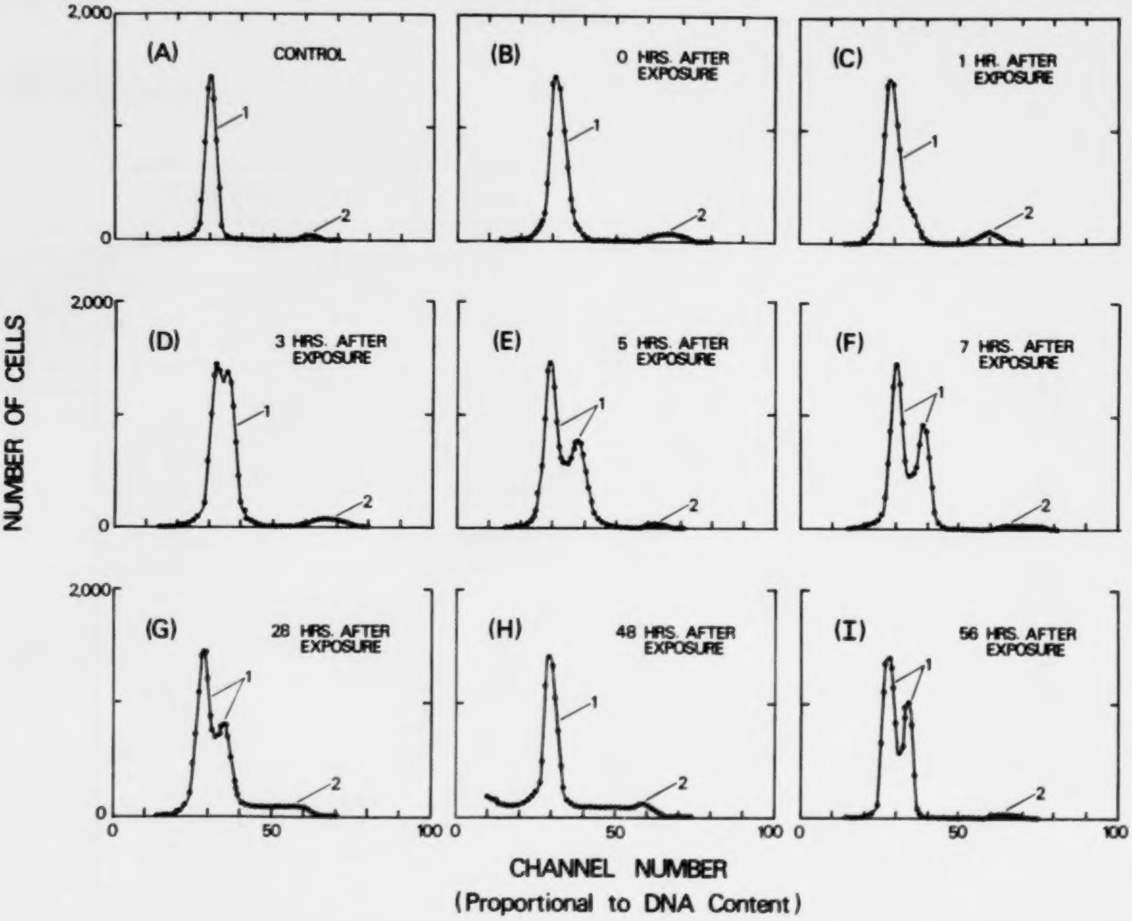

Figure 4. DNA content frequency distribution histograms of hamster respiratory tract cells fixed in ethanol (70%) and stained with mithramycin. Hamsters were exposed to 4 ppm of ozone for 4 hours prior to obtaining samples at increments ranging from 0 to 56 hours after exposure.

dyes having ultraviolet absorption ranges[4] and to analyze DNA content and protein in cells stained with mithramycin and rhodamine.[10] Mithramycin and rhodamine have violet and yellow excitation ranges, respectively, with overlapping emission spectra.[10] This measurement is made possible only through the use of dual-laser excitation. For example, hamster respiratory tract cells have been analyzed recently using this procedure, as illustrated in Figure. 5. Peak 1 of the DNA content distribution represents mononucleated cells (macrophages, leukocytes, etc.) having 2C DNA content and peak 2 binucleated cells and doublets (4C DNA content). Figure 5B, which represents the distribution of protein within the lung cell population, is broad and similar to that previously reported using the propidium iodide-fluorescein isothiocyanate method.[3] The nuclear and cytoplasmic diameter distributions are shown in Figs. 5C and 5D, respectively. Peaks 1 and 2 (cytoplasmic diameter distribution) have been identified recently as being composed of (a) leukocytes and (b) macrophages and epithelial cells, respectively. This new staining and analysis method has broad application in measuring the biochemical and cytological properties of respiratory tract epithelium.

Quantitation of Pulmonary Macrophage Phagocytosis

Phagocytic activity, which is the primary function of pulmonary macrophages, is normally measured by exposing test animals to toxic agents, followed by intratracheal injection of micron-sized polystyrene latex particles or bacteria for a fixed time period and lung lavage to remove macrophages, and microscopic enumeration of macrophages containing 1, 2, 3, etc., particles per cell. Described below is a new method to study the mechanisms of phagocytosis of alveolar macrophages from experimental animals exposed to toxicants using 1.83-μm diameter polystyrene latex (fluorescent) spheres. Figure 6A shows the fluorescence distribution of phagocytized and nonphagocytized spheres obtained from lavaging the respiratory tract. This distribution was obtained by recording the fluorescence signals from macrophage-ingested spheres and nonphagocytized particles. Peaks 1, 2, and 3 of Figure. 6A represent single macrophages that contain one sphere or a single sphere alone; single macrophages containing two spheres or two spheres stuck together (doublet); and single macrophages containing three spheres or three spheres stuck together (triplet), respectively. To distinguish between macrophages that have phagocytized spheres and nonphagocytized particles, the light-scatter method[6,9] for cell-size determination was used. Since 1.83-μm diameter spheres are much smaller than pulmonary cells, they did not appear in the cell-size distribution (Figure. 6B). Peak 1 is thought to be leukocytes and cellular debris. Peak 2 has been identified to represent macrophages that do and do not contain phagocytized spheres. Therefore, by requiring fluorescence signals to be or not to be in coincidence with light-scatter signals (cells), nonphagocytized spheres and macrophages that have phagocytized spheres can be distinguished. For example, Figure. 6C shows the fluorescence distribution of only macrophages that have ingested spheres as obtained by displaying only those fluorescence signals that also scatter light. Cells contained within peaks 1 to 5 (Figure. 6C) represent macrophages having phagocytized 1

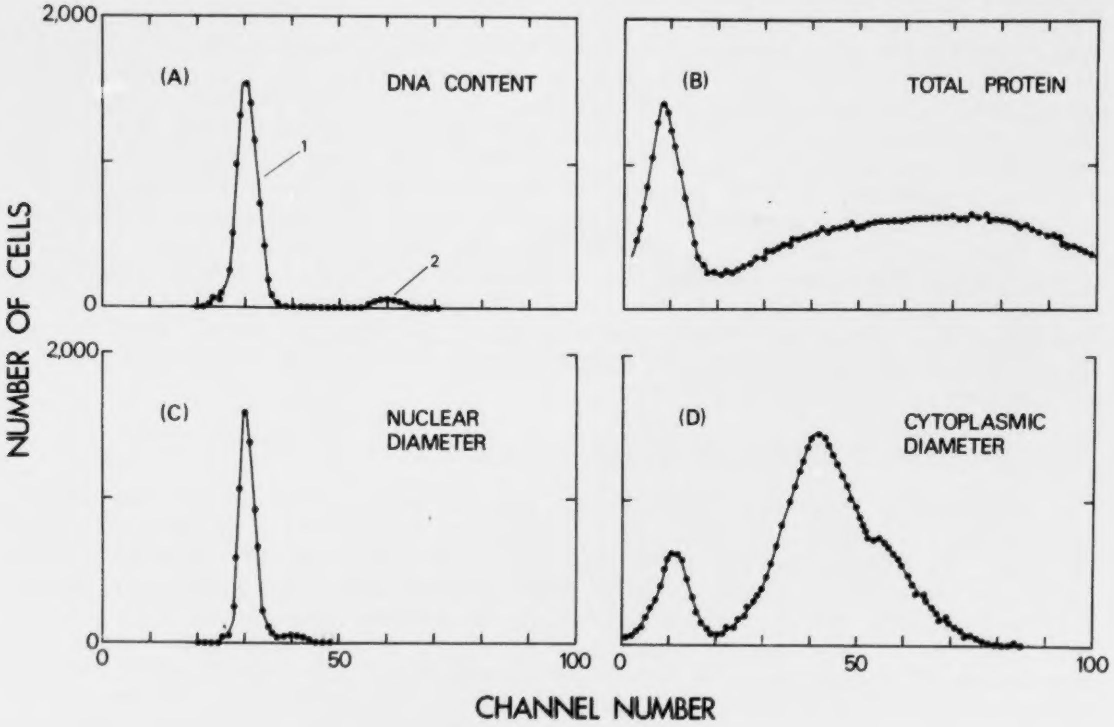

Figure 5. Frequency distribution histograms of normal hamster respiratory tract cells fixed in ethanol (70%) and stained with mithramycin (DNA content) and rhodamine 640 (total protein): (a) DNA content; (b) total protein; (c) nuclear diameter; and (d) cytoplasmic diameter. The nuclear and cytoplasmic diameter distributions were obtained by measuring the time durations of the fluorescence signals from the nucleus (mithramycin) and cytoplasm (rhodamine), respectively.

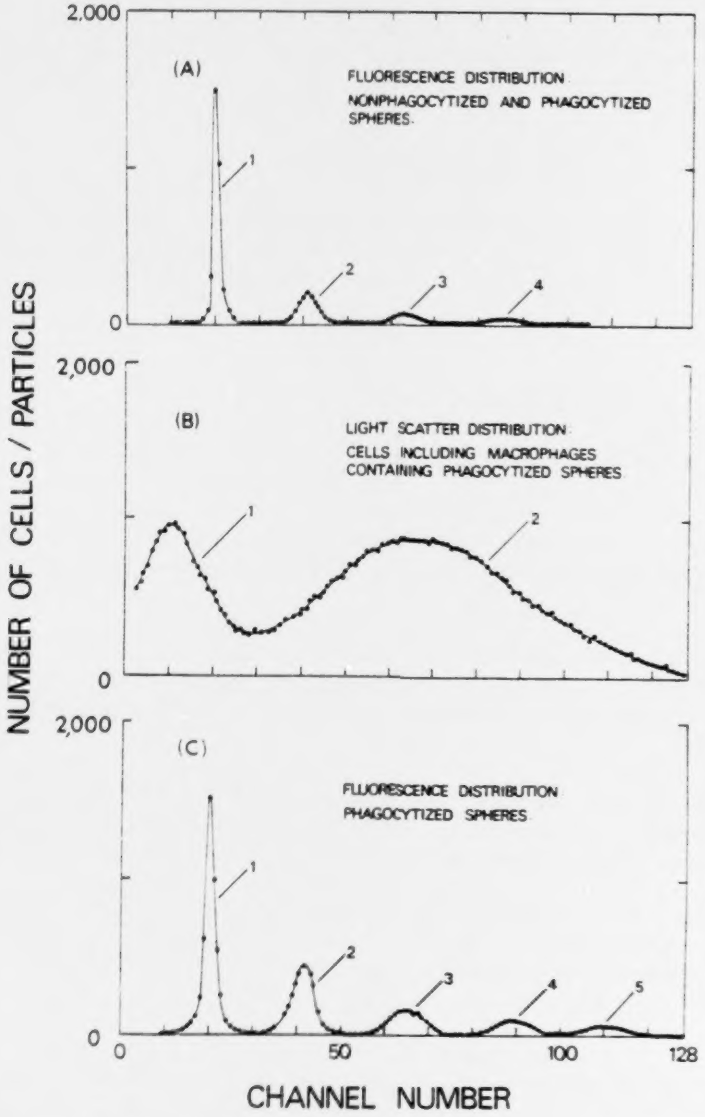

Figure 6. Frequency distribution histograms of microspheres and cells obtained by sacrificing normal rats and lavaging the lungs with saline 2 hours after instilling 1 to 2 x 10^7 1.83-μm diameter fluorescent spheres in 0.5 ml saline: (a) fluorescence distribution of nonphagocytized and phagocytized spheres obtained by recording all fluorescence signals; (b) light-scatter distribution (size) of cells, including macrophages containing phagocytized spheres; and (c) fluorescence distribution of phagocytized spheres obtained by recording only those fluorescence signals associated with light-scatter signals. Cells were fixed in 35% ethanol prior to fluorescence and light-scatter analysis.

to 5, respectively, as identified by sorting cells from each peak.[5] This technique has potential for permitting rapid and accurate determination of phagocytosis and will be used subsequently to assay for toxicity related to macrophage function.

ACKNOWLEDGMENTS

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BIOLOGICAL MONITORING METHODOLOGIES FOR OIL SHALE AREA SURFACE WATERS WITH EMPHASIS ON MACROINVERTEBRATE SAMPLING TECHNIQUES

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ABSTRACT

There exists a pressing need for reliable biological sampling methodologies applicable to streams of the semi-arid west. This is particularly relevant for rivers such as the White and Yampa which are potentially subject to nonpoint pollution impact as a result of oil shale and coal development.

The efficiency of two types of artificial substrate samplers (basket and multiple-plate), the Surber sampler, and variations of a traveling-kick method was evaluated for describing macroinvertebrate communities representative of the White River, Utah and Colorado. Basket samples provided the largest number of animals per sample, while the kick method provided data with the best statistical reproducibility. Multiple-plate and Surber samples provided highly variable results in terms of the number of animals and taxa collected. The kick technique was effective in riffle areas where the bottom fauna was particularly sparse and where a prohibitive number of Surber or multiple-plate samples would be required to adequately describe the benthic community.

INTRODUCTION

This paper addresses aspects of environmental monitoring that all too frequently are omitted in discussions of surface water quality monitoring requirements. We refer to the need to incorporate biological components into comprehensive water quality monitoring programs to broaden the spectrum and increase the efficiency of monitoring networks. In this paper we point out certain advantages to biological monitoring and address some of the approaches and associated problems. Although much of this discussion relates to aquatic biomonitoring as it applies regionally or nationally, particular emphasis is focused on an evaluation of methodologies for sampling aquatic macrobenthic communities in streams in the oil shale area.

The authors of the Federal Water Pollution Control Act Amendments of 1972 (PL 92-500) recognized the significance of aquatic organisms as natural monitors of water quality and recommended their use for that purpose. However, in an essay entitled, "Problems in Implementing U.S. Water Quality Goals," Westman[1] contended that biological monitoring requirements of PL 92-500 were not being met and attributed that failure in part to:

(1) the lack of biologically trained personnel at the monitoring sites;

(2) a long-standing bias toward chemical and physical rather than biological monitoring; and

(3) a lack of guidelines for conducting biological monitoring in receiving waters.

He further stated that neither EPA's Office of Research and Development nor the Department of Interior's Fish and Wildlife Service is conducting any research on development of biological monitoring methodologies.

From a national perspective, Westman is probably correct in his contention that biological monitoring in receiving waters is not being conducted at all places "where appropriate." The lack of biologically trained personnel at the monitoring sites is obviously a factor, but this is not due to a shortage of competent biologists. Rather it reflects the long-standing bias toward physical and chemical monitoring to which Westman refers in his second point. His third point, a lack of guidelines for conducting biological monitoring, is only partially justified. EPA has issued guidelines for biomonitoring in receiving waters in the form of manuals and numerous individual technical papers and has funded the development of many others. Furthermore, considerable research effort is being directed toward the development and refinement of biomonitoring methodologies by EPA.

As viewed from the standpoint of the analytical chemist, the state-of-the-art of biological monitoring is still quite primitive. The water quality biologist attempts to unravel the complexities of a highly intricate system in an effort to determine if observed changes in the biota are real and, if so, whether these changes can be attributed to man-made influences. Consequently, additional research must be directed towards the development of new techniques and the refinement of existing methodologies in a continuing effort to describe the most cost-effective methodologies for specific monitoring applications.

BIOLOGICAL MONITORING

ADVANTAGES

Foreign materials introduced into an aquatic environment interact in a complex and often non-linear manner with one another and with the numerous other factors inherent to the environment.[2] Aquatic organisms and communities respond to the sum of the interactions of these environmental factors. Thus, biomonitoring is particularly well suited to detecting changes in ambient conditions caused by both suspected and unsuspected foreign materials, even though the actual cause-effect relationships may be too complex to readily evaluate.

An additional and very significant advantage of biological monitoring is that it provides a mechanism for the integration of conditions between sampling periods. Aquatic communities are affected by short-lived perturbations of the environment and these effects normally persist for the weeks or months required for the communities to recover.[3] Thus, periodic biomonitoring can be used to detect short-term events, which chemical/physical monitoring is unlikely to detect. Biological monitoring, then, is especially advantageous because it will detect the full spectrum of suspected and unsuspected impacts including manifestations of intermittent insults even through periodic sampling. Pollution is fundamentally a biological problem. We monitor certain chemical-physical parameters primarily because we know or suspect that they directly or indirectly affect living organisms.

APPROACHES

Biological monitoring generally approaches the recognition or detection of problems in aquatic systems by three basic types of measurements: 1) toxicity of pollutants both in the field and laboratory; 2) bioconcentration; and 3) community composition and structure.

Measurements of the toxicity of pollutants provide information on the effects of their exposure upon living organisms. Such measurements can be conducted in a laboratory under closely controlled conditions, or in the field under ambient conditions. There are advantages and disadvantages to both approaches. Laboratory environments are easily controlled, but do not precisely simulate field conditions. Results obtained in the laboratory are thus of limited value as predictors of the impacts of pollutants when applied to the "real-life" conditions of a specific environment.[4] Field measurements of toxicity (e.g., caged animals placed in an outfall or receiving stream) are direct in their approach, but are subject to vandalism, flooding, and a host of other uncontrollable factors including exposure of test organisms to unknown constituents and dosages for indefinite periods of time. Feedback between laboratory and field studies will, on the one hand, aid in the refinement of toxicity tests and, on the other hand, add light to the information collected in the field. In an optimal monitoring program, laboratory testing would be complemented by field studies designed to assess the actual impacts of particular substances or combinations of substances on organisms within a particular environment.

The results of toxicity studies may be readily apparent, as in acute tests which result in the death of a percentage of test organisms that are exposed for a finite period to known concentrations of a particular substance (e.g., LC_{50}), or tests in which caged test organisms die when exposed to an effluent. More frequently, however, responses are less pronounced and result in alterations of physiological or behavioral responses such as respiration rate, movement, reproductive success, incidence of tumors, etc. Chronic exposure to low-level concentrations may have no measurable effect on the test organisms themselves, but the effect of exposure may be manifested several generations later, in the form of abnormalities resulting therefrom.

The second biomonitoring approach utilizes the characteristic of living organisms to act as natural compositors and integrators of substances from the surrounding water medium. Plants and animals accumulate and concentrate substances in tissue through bioaccumulation (uptake from the water) and biomagnification (uptake through the food chain). The uptake characteristics of organisms vary by individual, species and trophic level. Ideally, receptors at several trophic levels would be included in bioconcentration studies. The most obvious advantage of bioconcentration studies is that they provide detection of hazardous materials at levels below analytical limits and suggest the potential hazard to various food chain components, including man. Thus, these analyses offer an efficient means for screening and identifying potentially hazardous substances in water before they pose a serious detriment to human health and aquatic life.

The third type of measurement--one in which the Environmental Monitoring Systems Laboratory (EMSL-LV) is very directly involved--is the response of aquatic communities to pollution-induced stress. It is difficult to obtain reliable measurements of this type because of the need to sample highly variable populations where composition and structure are subject to all the perturbations of the environment, both natural and man-induced. For example, immature aquatic insects (which are the most prominent organisms in most macrobenthic samples from streams of semi-arid regions) are highly sensitive to pollution-induced stress conditions, but they also show large natural seasonal variations due to characteristics of their life cycles and natural fluctuations in stream conditions. In addition, identification of many groups of these insects poses special problems, due largely to the lack of taxonomic information on their immature stages. In spite of the difficulties involved in characterization of aquatic communities, be they fish, invertebrates or plant life, carefully planned and executed investigations are well worth the effort. They offer a fairly efficient means of detecting pollution-induced stress once the natural community patterns have been fully described.

INTEGRATION WITH PHYSICAL-CHEMICAL MONITORING

The use of biological monitoring to complement physical-chemical approaches is particularly advantageous for instream monitoring in the oil shale area. Developmental activities will most likely result in nonpoint-source impacts via landscape disturbances, diffusion through ground water, and fallout from the atmosphere. In addition, accidental spills and discharges pose a substantial threat. A strictly physical-chemical monitoring network that would monitor all suspected pollutants continually and throughout the stream reaches of the potentially affected area would be very difficult and expensive to operate and could still fail to detect unsuspected or low-level pollutants. However, periodic biological samples, collected from strategically located stations, could detect pollution-induced changes in the biota and provide an alert to hazardous conditions. In response to such an alert, intensive physical-chemical monitoring could pinpoint both the "danger spots" and the causative agents and sources. As additional information becomes available concerning the relationships between specific pollutants and specific changes in the biota, the identification of the pollutants and their sources will become easier. Only the complementary use of biological and physical-chemical monitoring will make it feasible to detect impacts and their sources over entire stream systems.

COMMUNITIES MOST SUITABLE FOR MONITORING

The stream communities in the oil shale area most appropriate for monitoring are the benthic macroinvertebrates owing to their ease in sampling, low mobility and ubiquitous distributions. The high mobility of fish not only increases the difficulty of collecting reproducible samples, but often enables the fish to avoid temporary perturbations, reducing their effectiveness as monitors of short-term events. Benthic organisms, on the other hand, are relatively stationary and have been demonstrated to respond in a measureable way to even very slight and periodic pollutant "leakages" to the environment.[5] Phytoplankton and aquatic vascular plants are of minor significance in streams of the oil shale area where periphyton are the primary producers.

MACROINVERTEBRATE SAMPLING TECHNIQUES

Although the accurate measurement of standing crop and absolute community composition of stream macroinvertebrates may be desirable, it has seldom been achieved in aquatic investigations. In fact, it has been demonstrated that conventional sampling techniques do not accurately measure these parameters.[6] Biological water quality investigations, however, are primarily comparative in nature, measuring spatial and temporal changes in community composition and structure. Therefore, the reduction in variability of estimates is of primary significance. Although it is not generally valid to compare standing crop and community composition estimates resulting from different types of collection techniques, it is meaningful to compare the variabilities associated with these techniques, and thus, their relative potential for collecting reproducible data sets.[7]

Probably the most widely used conventional stream macroinvertebrate sampling device is the Surber square-foot sampler. High sample-variability and species-selectivity has been associated with this method.[8,9] An improved modification of the Surber sampler is the enclosed box sampler which prevents loss of organisms due to backwash.[10] Both of these samplers, however, are restricted to use in riffle areas with water depths of under 30 centimeters.[11] Furthermore, they have the disadvantage of collecting from small areas of substrate (0.1 square meter); therefore, they require large numbers of replicate samples to adequately characterize communities which exhibit sparse or patchy distributions. Artificial substrates such as the multiple plate and basket samplers have been effectively used in large streams to reduce sample variability by more accurately defining the actual area of habitat sampled.[12,13] However, these devices are of limited utility in streams of the arid and semiarid regions which are characterized by highly irregular flow patterns and heavy sediment loads. Our experience with both types of artificial substrates in these waters has been very discouraging. During high flow periods, the samplers are often swept away, badly clogged with debris or even buried by sediments. As the water level recedes, suspended samplers are often left exposed above the water line. In addition, artificial substrates are highly susceptible to vandalism.

TESTS OF MACROINVERTEBRATE MONITORING TECHNIQUES

In an effort to assess the utility and limitations of the various macroinvertebrate sampling methodologies, considerable testing was conducted in the lower and intermediate reaches of the White River during 1975-78 in a wide range of habitats and river conditions. These studies have been described in several technical reports.[14,15,16] Some of the more significant results are discussed below.

SAMPLING STATIONS

Five stations in the vicinity of the U-a/U-b federally leased oil-shale tracts were sampled during 1975-76 (Figure 1). This portion of the river flows through arid, sparsely vegetated country and is characertized by irregular flow patterns, highly turbid waters, and unstable bottom substrates. As a result of these conditions, the bottom fauna is often very sparse, which greatly limits the usefulness of conventional, small-area sampling methods.

Collections were also taken during 1977 and 1978 at three stations in the Colorado portion of the river. Two stations were located in the vicinity of the Piceance Creek confluence and the third station was located 12 kilometers upstream from Meeker (Figure 1). The bottom substrates at these stations were more stable than those at the Utah stations and supported much greater densities of macroinvertebrates. Under such conditions, small-area samplers collected greater numbers of organisms, and thereby provided more information and more reliable data sets than in the unstable substrate near the U-a/U-b tracts.

TECHNIQUES EVALUATED

A standard Surber sampler, as supplied by Wildlife Supply Company, was used to collect samples from the White River, Utah, during fall, 1975. For subsequent sampling, the original net (68-cm long with 10 strands/cm) was replaced with a net 90-cm long with 12 strands/cm (30 mesh). It was assumed

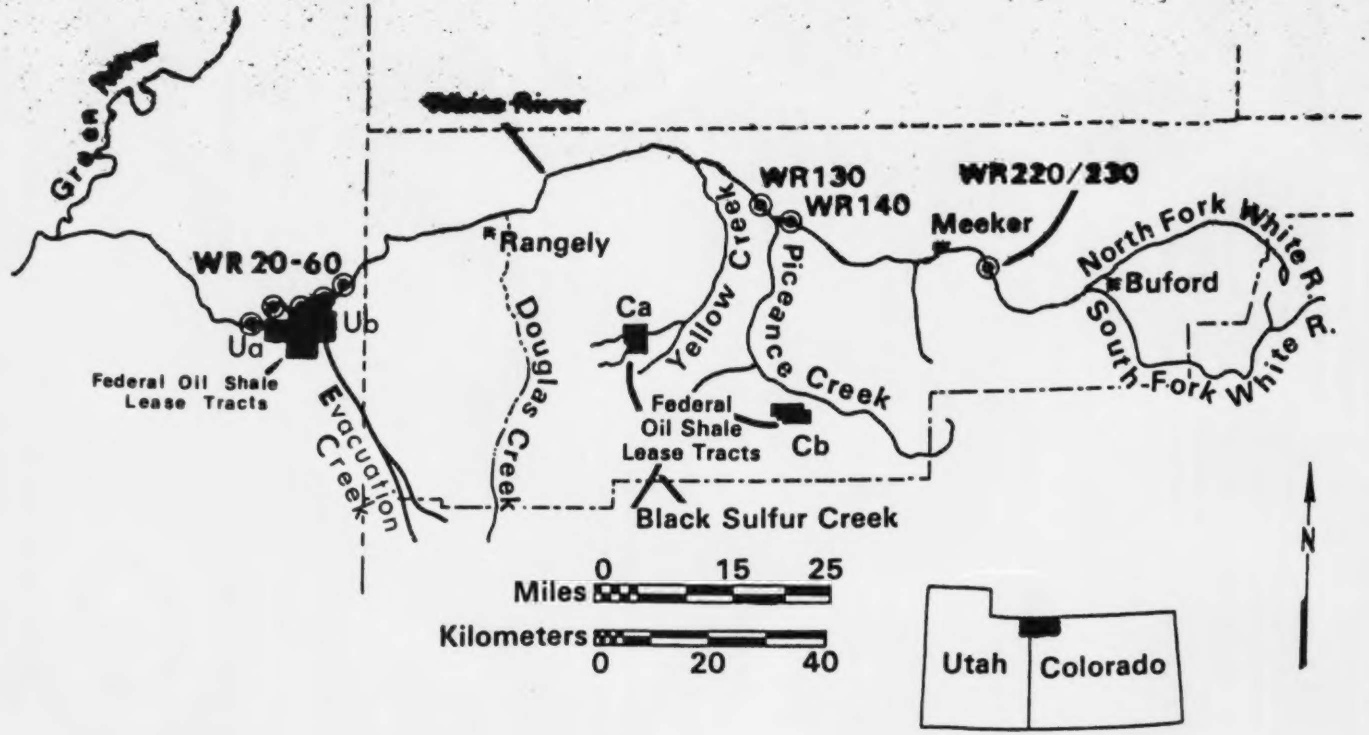

Figure 1. Map of the study area showing location of the White River sampling stations and oil shale tracts.

that the longer net would reduce backwash and the finer netting allow entrapment of the smaller macroinvertebrates.

Collections with an enclosed Portable Invertebrate Box Sampler (PIBS), supplied by Ellis-Rutter Associates, were included during the 1977 and 1978 investigations. This enclosed-box sampler collects from 0.1 square meter (m^2) of bottom substrate and was supplied with a 76-cm-long, 30-mesh net.

A Standardized Traveling Kick Method (STKM) which consists of holding a net at arms length and traveling slowly downstream while vigorously kicking the substrate was also utilized. All kick samples were standardized in terms of length of time the net was held in the water and the distance of downstream travel.

One-minute traveling kick samples were collected during spring 1976, with a round, conical-shaped, 50-cm-long, coarse-mesh dip net with a 25-cm mouth opening. All other traveling kick samples were collected with a triangular, 76-cm-long nylon dip net. Forty-mesh netting was used for the fall 1976 collections and 30 mesh netting was used for the 1977 and 1978 collections. The triangular kick nets had a mouth opening of 28 cm by 28 cm by 24 cm. The 30-second kick samples were collected from areas of approximately 3/4 by 4 meters (3 m^2), while the one-minute collections were taken from areas approximately 6 m^2.

Two types of multiple-plate samplers were used in the study. During the fall of 1975, multiple-plate samplers used consisted of nine hardboard plates, evenly spaced 0.4 cm apart to provide a total surface area of 0.11 m^2. A 45-cm all-thread bolt, inserted through the center of the plates and spacers, held the assembly together. The multiple plate samplers used in 1976 were constructed as described in the U.S. EPA Biological Field and Laboratory Methods Manual.[17] These samplers, which consisted of 14, 7.5 cm diameter unevenly spaced circular plates, provided a total surface area of 0.12 m^2. Both types of samplers were secured in the stream by driving them into the substrate and were retrieved 4 to 6 weeks after placement.

Basket samplers utilized were cylindrical, chrome-plated, wire barbeque baskets, 17 cm in diameter and 26 cm in length. These were filled with cleaned rocks from the stream bank and placed on rocky areas of the stream bottom. Baskets remained in the stream 4, 6 or 8 weeks before retrieval.

Although both 40- and 30-mesh nets were used to collect STKM samples during 1976, all samples were washed in a 30-mesh sieve to obtain consistent minimum organism size from sample to sample.

COMPARISON OF TECHNIQUES

Various combinations of techniques were tested in both the Utah and Colorado reaches of the White River to investigate their relative performance in fauna-poor and fauna-rich areas. All sampling was confined to riffle areas of the stream. The number of replicates for each set varied. In order to facilitate direct comparison between sampling methodologies, most sample sets were collected by the various methods from sites identical or adjacent to each other. Each sample set represented a group of replicate samples specific for a given combination of site, date and method.

Standardized traveling-kick samples generally provided relatively large numbers of organisms per sample with the least variability of the five sampling methods tested (Tables 1 and 2). Mean coefficients of variation for the numbers of organisms collected within sample sets ranged from 42 to 78 for Surber and PIBS samples and 30 to 37 for kick samples. The relatively low variability between samples within kick-sample sets was most evident for those collected from the fauna-poor lower-river stations (Utah), where the mean coefficients of variation ranged from 36 to 37 for the STKM sample sets and 68 to 78 for the Surber sample sets. Multiple-plate and basket samplers yielded intermediate sample-to-sample variability (Table 2). For purposes of community composition estimates, kick samples generally collected higher numbers of taxa per sample with lower between-sample variability than the other sampling methods (Tables 1 and 2). In addition, the traveling kick samples yielded the lowest between-sample variability for Shannon-Weiner diversity values (Table 2).

Of the four methods tested in Utah for similarity in species composition, the samples obtained with the kick and Surber method most nearly approximated one another. However, this was not the case with calculated diversity indices. Close comparisons of the species composition of these two methods reveal that the kick method selected more heavily for the loosely attached baetid mayflies, while the Surber sampler selected more heavily for the closely attached black flies. However, most species collected by Surber samples were also collected by kick samples, and, in fact, individual kick samples collected, on the average, 3 to 5 more taxa than did Surber samples (Table 1). Relative selectivities of methods were also demonstrated in the Colorado collections; the Surber and PIBS methods generally yielded higher proportions of the closely attached organisms than did the kick method.

The primary purpose of community analyses in water-quality investigations is the detection and quantification of changes in the biological components of the aquatic ecosystem resulting from physical and chemical alterations in the aquatic environment. The STKM was observed to be considerably more efficient for sampling the unstable, fauna-poor substrates of the lower White River, Utah, than the other methods tested. In addition, the kick method compared favorably with the conventional small-area Surber and PIBS methods in the fauna-rich riffles of the upper White River, Colorado. Thus, although the STKM shows its greatest usefulness in the downstream reaches of the river, its favorable performance in the upper reaches enables direct comparisons between fauna-rich and fauna-poor stations. The kick method is also applicable across a broader range of stream depths than the Surber method. This extended flexibility of the STKM makes it the method of choice particularly during high flow periods, when mainstream shallow riffles are unavailable for Surber or PIBS sampling.

TABLE 1. TOTAL NUMBER OF SAMPLES (n), MEAN NUMBER OF ORGANISMS ($\overline{X}A$), MEAN NUMBER OF TAXA ($\overline{X}T$), AND MEAN SHANNON DIVERSITY INDEX ($\overline{X}H$) FOR FIVE MACROINVERTEBRATE SAMPLING METHODS

River Season-Year	Surber				PIBS				Traveling Kick				Multiple Plate				Basket			
	n	$\overline{X}A$	$\overline{X}T$	$\overline{X}H$	n	$\overline{X}A$	$\overline{X}T$	$\overline{X}H$	n	$\overline{X}A$	$\overline{X}T$	$\overline{X}H$	n	$\overline{X}A$	$\overline{X}T$	$\overline{X}H$	n	$\overline{X}A$	$\overline{X}T$	$\overline{X}H$
White River, Utah, Fall, 1975	80	28	6	1.8	--	--	--	--	--	--	--	--	21	27	7	2.0	3	112	10	2.3
White River, Utah, Spring, 1976	48	114	8	1.8	--	--	--	--	34*	221	11	2.0	16	155	9	1.8	4	716	15	1.8
White River, Utah, Fall, 1976	95	104	10	2.8	--	--	--	--	135	276	15	2.8	12	29	9	2.6	11	121	13	2.9
White River, Colorado, Fall, 1977	10	584	21	2.7	--	--	--	--	10	1074	26	2.9	--	--	--	--	--	--	--	--
White River, Colorado, Spring, 1978	5	654	15	2.0	15	750	18	2.5	15	1161	18	2.5	--	--	--	--	--	--	--	--

TABLE 2. NUMBER OF SAMPLE SETS (n), NUMBER OF REPLICATES PER SAMPLE SET (r), AND THE MEAN COEFFICIENT OF VARIATION OF THE SAMPLE SETS FOR NUMBER OF ORGANISMS (A), NUMBER OF TAXA (T), AND SHANNON DIVERSITY INDEX (H)

River Season-Year	Surber					PIBS					Traveling Kick					Multiple Plate					Basket				
	n	r	A	T	H	n	r	A	T	H	n	r	A	T	H	n	r	A	T	H	n	r	A	T	H
White River, Utah, Fall, 1975	8	10	68	39	34	--	--	--	--	--	--	--	--	--	--	4	4-6	51	32	35	--	--	--	--	--
White River, Utah Spring, 1976	6	8	68	25	14	--	--	--	--	--	4*	4-10	36	19	13	4	4	52	17	17	--	--	--	--	--
White River, Utah, Fall, 1976	7	10-15	78	35	26	--	--	--	--	--	9	10-15	37	17	8	1	12	56	44	31	1	6	48	27	15
White River, Colorado, Fall, 1977	2	5	47	13	4	--	--	--	--	--	2	5	30	13	4	--	--	--	--	--	--	--	--	--	--
White River, Colorado, Spring, 1978	1	5	42	15	16	3	5	45	19	15	3	5	32	14	6	--	--	--	--	--	--	--	--	--	--

*60-second traveling kick samples were collected in spring, 1976, and 30-second traveling kick samples were collected on all other dates.

Results from this study indicate that the standardized traveling-kick method, when used as described, is the most efficient technique for sampling stream benthos in semi-arid regions such as the western oil shale area. This method is particularly effective where and when faunal patchiness and paucity render more conventional small-area sampling methods impractical.

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THE BIOLOGY OF A PLAINS STREAM, SALT WELLS CREEK, IN AN OIL SHALE AREA, SOUTHWESTERN WYOMING

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Salt Wells Creek typifies plains streams draining extensive oil shale areas of southwestern Wyoming. The stream is intermittent but has several small tributaries in its headwaters that are perennial due to springs. Springs and perennial reaches support an abundant aquatic community, including several species of small fish. Aquatic organisms found in downstream intermittent reaches are generally washed in from upstream. Some invertebrates survive dry periods by burrowing into the streambed.

Each of the three stream environments--ponds, springs, and perennial reaches--contains distinct invertebrate communities. Green and bluegreen algae are dominant during high streamflow. Diatoms are dominant during low streamflow. Seasonal succession of community development occurs in periphyton and benthic invertebrates. Amphipods and caddisflies are the principal benthic invertebrates. Aquatic organisms in plains streams survive through periods of relatively high temperature and high concentration of suspended sediment and dissolved solids.

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AQUATIC TOXICITY TESTS ON INORGANIC ELEMENTS OCCURRING IN OIL SHALE

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ABSTRACT

Using the rainbow trout (Salmo gairdneri), embryo-larval toxicity tests were performed on 33 elements which occur in oil shale and other fossil fuels. Continuous exposure was maintained from fertilization through 4 days posthatching, employing static renewal procedures and test responses were based on lethality and teratogenesis. The LC_{50}s were under 1.0 mg/l for 19 of the 33 elements, indicating high sensitivity of developmental stages of the rainbow trout to a wide range of elements which occur in oil shale, spent shale, and process waters. Elements which proved most toxic to trout eggs and larvae were Hg, Ag, La, Ge, Ni, Cu, and Cd, with probit-derived LC_{50}s of 0.005, 0.01, 0.02, 0.05, 0.05, 0.11, and 0.14 mg/l, respectively.

Exposure levels which produced 1% control-adjusted impairment of test populations (LC_1) were also determined by log probit analysis, to provide a basis for estimating threshold concentrations. The LC_1 values were at or under 10 μg/l for 12 elements, including Ag, Be, Cd, Cu, Ge, Hg, La, Ni, Pb, Tl, V, and Zr. To determine reliability of the LC_1 values, they were compared with maximum acceptable toxicant concentrations developed in continuous flow embryo-larval and chronic reproductive studies and with current freshwater criteria. Good correlations generally were obtained where data were adequate to permit comparisons. Results showed that static renewal tests with trout embryo-larval stages afforded a reliable and economical means of screening oil shale contaminants for toxic properties, identifying those of greatest concern to aquatic ecosystems, and estimating concentrations which may produce hazardous effects. To assist further in prioritizing elements for studies on environmental monitoring and biological effects, oil shale, spent shale, and retort waters were compared for elemental composition.

Trout embryo-larval tests also were conducted on simple metal mixtures, to evaluate possible antagonistic, additive, or synergistic interactions. Mercury was mixed in equal proportions with each of three other metals, including cadmium, copper, and selenium. Analysis of dose-response data clearly indicated that the type of interaction varied with concentration. At lower exposure levels, copper-mercury was antagonistic, and the other

mixtures were additive to antagonistic. All mixtures became synergistic at or above median lethal concentrations. As synergism was dependent on high exposure levels, this interaction appeared less likely to be significant under ambient conditions.

INTRODUCTION

Upwards of 65 elements reportedly occur in oil shale, and spent shale and retort waters contain significant concentrations of many elements considered hazardous to aquatic biota.[1 2 3] Environmental outfall of inorganic contaminants may approach or equal that observed for coal. Using data from recent investigations,[1-18] the composition of oil shale, coal and their waste products was compared for 33 of the elements which may prove detrimental to aquatic life (Table 1). Utilization of oil shale will yield a high ratio of waste products, averaging about 91 tons of spent shale and 400 to 3,000 liters of retort water for every 100 tons of shale processed.[4] Aqueous leaching of solid wastes may constitute the principal threat to surface and groundwaters, particularly as retort and other wastewaters may be used in wetting down spent shale.[4] Fallout from atmospheric discharges also may reach aquatic ecosystems, including waters affected by local deposition flux, atmospheric scavenging, and terrestrial runoff.[5,19,20] The Green River oil shale formation covers approximately 17,000 square miles in Colorado, Utah, and Wyoming, and reserves have been calculated at 600 billion barrels of oil, considering only that shale estimated to yield a minimum of 25 gallons of oil per ton.[6] Due to the potential magnitude of this new energy technology and the expansive geographic regions which will be affected, it is essential to establish waste disposal guidelines which will ensure environmental acceptability.

However, definitive freshwater criteria have been slow to develop and currently exist for only a small fraction of the elements found in oil shale. If an adequate data base for hazard assessment is to be achieved within the time frame contemplated for the implementation of oil shale technology, it is essential to develop a more rapid and economical means of delineating guidelines for waste disposal. McKim[21] recently reviewed data for a wide range of aquatic toxicants and concluded that continuous flow fish embryo-larval tests which extended beyond hatching by 30 days or more yielded responses comparable to those produced in chronic life-cycle studies. As suggested by McKim, this affords a somewhat more economical procedure for estimating maximum acceptable toxicant concentrations (MATC). In addition, continuous flow embryo-larval tests of even shorter duration have produced sensitivity equal to that observed with chronic testing procedures.[22-24] However, considering the many aquatic contaminants which may result from new energy technologies, still simpler and more rapid screening procedures are required.[25] In this investigation, static renewal toxicity tests with embryos and larvae of the rainbow trout were used (1) to compare toxicity of 33 elements which occur in oil shale, (2) to identify particularly hazardous elements for more comprehensive study, and (3) to provide a basis for estimating initial freshwater guidelines in instances where established criteria are lacking.

Table 1. CONCENTRATIONS (ppm) OF TOXIC ELEMENTS OCCURRING IN OIL SHALE, COAL, AND THEIR WASTE PRODUCTS

Element	Oil Shale	Spent Oil Shale	Oil Shale Retort Water	Coal	Ash Pond Effluent	Coal Conversion Process Waters
Aluminum	5000 - >10000	-	0.11 - 0.66	4300 - 30400	1.4 - 7.2	0.007 - 3
Antimony	0.20 - 11	1	0.004 - 0.036	0.2 - 8.9	-	0.007 - 0.5
Arsenic	2.6 - 108	15	4.6 - 10	0.5 - 106	0.005 - 0.038	0.001 - 1
Barium	32 - 750	180	0.002 - 0.22	33 - 750	0.1 - 0.3	0.02 - 0.1
Beryllium	0.26 - 35	0.3	-	0.2 - 31	<0.01 - 0.01	<0.02 - 0.02
Boron	12 - 140	53	4.4 - 8.8	1.2 - 356	-	0.4 - 82
Cadmium	0.02 - 1.4	≤0.8	-	0.1 - 65	0.001 - 0.037	0.01
Cesium	0.06 - 11	7	0.002 - 0.007	0.49 - 1.5	-	<0.005 - 0.01
Chromium	21 - 1000	125	0.011 - 0.037	0.3 - 610	0.004 - 0.067	0.004 - 0.6
Cobalt	0.78 - 39	11	0.002 - 0.65	0.5 - 43	-	0.002 - 0.5
Copper	15 - 120	48	0.007 - 0.16	1.8 - 185	0.01 - 0.31	0.002 - 5.0
Gallium	1.1 - 18	14	-	1.1 - 61	-	<0.005
Germanium	0.37 - 2.9	0.65	0.001 - 0.007	1.0 - 819	-	0.001 - 0.01
Lanthanum	1.1 - 50	20	0.002 - 0.010	3.3 - 98	-	0.05 - 0.46
Lead	1.0 - 70	19	0.062 - 0.37	4 - 218	0.01 - 0.06	0.002 - 1.0
Lithium	1.9 - 850	160	0.004 - 0.75	3.1 - 25	-	0.001 - 0.020
Magnesium	5000 - >10000	-	5.3 - 8.7	100 - 2500	0.4 - 14	0.32 - 50.0
Manganese	9 - 390	405	0.042 - 0.14	6 - 181	0.01 - 0.58	0.01 - 15.0
Mercury	0.2 - 1.4	-	<0.1 - 0.1	0.01 - 1.6	0.0002 - 0.038	0.007 - 0.030
Molybdenum	4.9 - 87	.6	0.056 - 0.340	1.0 - 73	-	0.001 - 0.5
Nickel	28 - 760	15	0.37 - 2.6	0.4 - 104	0.05 - 1.1	0.001 - 10.0
Selenium	0.08 - 5.2	1	0.003 - 0.98	0.4 - 7.7	0.002 - 0.065	0.002 - 0.3
Silver	0.04 - 1.7	1.7	0.002 - 0.230	0.03 - 0.19	<0.01 - 0.01	<0.02
Strontium	59 - 2700	460	0.003 - 0.48	10.0 - 37	-	0.015 - 0.120
Tantalum	0.04 - 4.8	<0.2	-	0.25	-	≤0.1 - 0.3
Tellurium	0.11 - 0.35	<0.2	0.001	0.5	-	<0.003
Thallium	0.3 - 1.4	<0.2	-	0.29 - 2.0	-	<0.003
Tin	0.11 - 11	1.5	8.9 - 100	1.0 - 51	-	<0.02 - 0.1
Titanium	150 - 2600	-	0.64 - 21	20 - 3200	-	0.003 - 0.3
Tungsten	0.03 - 2.9	1.25	0.003 - 0.024	0.04 - 3.0	-	0.03 - 0.07
Vanadium	10 - 280	135	0.004 - 11	10 - 1281	-	0.001 - 0.033
Zinc	12 - 136	35	0.26 - 0.47	15 - 5600	0.03 - 1.51	0.007 - 5.0
Zirconium	3.0 - 60	110	0.008 - 0.390	8 - 133	-	0.02 - 0.1

MATERIALS AND METHODS

Embryo-larval toxicity tests were performed with the rainbow trout (Salmo gairdneri), using static renewal procedures previously described by Birge et al.[26] Test water and toxicant were changed at regular 12-hour intervals. Treatment was maintained continuously from fertilization through 4 days posthatching, giving an exposure period of 28 days. Water hardness ranged from 92 to 110 mg/l $CaCO_3$, and pH varied from 6.9 to 7.8. Moderate aeration was used to maintain dissolved oxygen within a range of 9.3 to 10.1 mg/l. A minimum of 7 mg/l has been recommended for trout and salmon spawning waters.[27] Other physicochemical characteristics of the test water have been described by Birge et al.[22] All tests were conducted in environmental rooms and temperature was maintained at 12° to 13°C. Test populations were examined each day to tabulate frequencies of lethality and teratogenesis. Log probit analysis was used to determine control-adjusted LC_1, LC_{10}, and LC_{50} values with 95% confidence limits. The lethal concentrations were determined with the method of Finney,[28] rather than the procedure of Daum[29] used in earlier investigations.[3,26] Teratic survivors, as described by Birge and Black,[30] were counted as lethals in probit calculations. Minimum sample size was set at 100 eggs, using 500-ml exposure chambers.

Elements and compounds selected for testing are given in Table 2. Hydrated salts were used for Al, Ba, Cd, Co, Cu, Fe, Mg, Mn, Mo, Ni, Sr, and Te. Concentrations of elements contained in prepared test solutions added to exposure chambers were confirmed with a Perkin-Elmer atomic absorption spectrophotometer (Model 503), equipped with an HGA 2100 graphite furnace and a mercury analyzer.[3,31] Test water was monitored for temperature, dissolved oxygen, water hardness, and pH, using a YSI telethermometer with thermocouple, YSI oxygen meter (Model 51A), Orion divalent cation electrode, and a Corning digital pH meter (Model 110).

RESULTS AND CONCLUSIONS

Tests conducted on embryonic and larval stages of the rainbow trout are summarized in Table 2. Median lethal concentrations (LC_{50}) and other values (LC_{10}, LC_1) were based on control-adjusted responses (lethality, teratogenesis) incurred during the 28-day expsoure period. Control populations, maintained simultaneously with experimentals, survived at frequencies ranging from 83% to 96%. The LC_{50}s were under 1.0 mg/l for 19 of the 33 elements, indicating high sensitivity of developmental stages of the rainbow trout to a wide range of elements which occur in oil shale and coal. Mercury, silver, and lanthanum were the most toxic. Of the remaining 14 elements, LC_{50}s ranged from 1.1 to 7.3 mg/l for Zr, Zn, Mn, Ga, Ta, Se, and Ti, and those elements which exhibited the lowest toxicity, based on median lethal concentrations, included B, Ba, Cs, Li, Mg, Te, and W. The high sensitivity of rainbow trout embryos and alevins has been noted in numerous previous investigations.[26,32-34] In particular, McKim et al.[34] observed life-cycle stages of the rainbow trout to be more susceptible to copper than were those of seven other fish species. Considering the LC_{50}s given in Table 2, a number of toxic elements occur in oil shale, retort waters, and

Table 2. TROUT EMBRYO-LARVAL BIOASSAYS ON ELEMENTS OCCURRING IN OIL SHALE

Test Element	LC_{50} (mg/l)	95% Confidence Limits	LC_{10} (µg/l)	95% Confidence Limits	LC_1 (µg/l)	95% Confidence Limits
Mercury ($HgCl_2$)	0.005	0.004 - 0.005	0.9	0.7 - 1.2	0.2	0.1 - 0.3
Silver ($AgNO_3$)	0.010	0.008 - 0.011	0.9	0.7 - 1.2	0.1	0.1 - 0.2
Lanthanum ($LaCl_3$)	0.02	0.01 - 0.03	3.7	2.3 - 5.2	0.9	0.4 - 1.5
Germanium (GeO_2)	0.05	0.04 - 0.05	2.8	1.9 - 3.8	0.3	0.2 - 0.5
Nickel ($NiCl_2$)	0.05	0.04 - 0.06	10.6	7.4 - 13.9	3.0	1.7 - 4.5
Copper ($CuSO_4$)	0.11	0.09 - 0.14	16.5	10.1 - 23.7	3.4	1.6 - 5.9
Cadmium ($CdCl_2$)	0.14	0.13 - 0.16	29.2	22.8 - 36.1	8.0	5.4 - 10.9
Vanadium (V_2O_5)	0.17	0.14 - 0.21	33.8	22.0 - 46.8	9.0	4.7 - 14.6
Thallium ($TlCl_3$)	0.18	0.14 - 0.22	36.3	24.0 - 50.0	9.9	5.2 - 15.8
Chromium (CrO_3)	0.19	0.15 - 0.23	56.9	34.6 - 80.2	21.5	10.3 - 35.2
Lead ($PbCl_2$)	0.22	0.19 - 0.25	40.9	31.1 - 51.4	10.3	6.9 - 14.6
Strontium ($SrCl_2$)	0.25	0.20 - 0.30	49.0	32.0 - 67.7	13.0	6.7 - 21.2
Beryllium ($BeCl_2$)	0.38	0.26 - 0.53	42.0	19.8 - 72.1	7.0	2.2 - 15.5
Tin ($SnCl_2$)	0.42	0.35 - 0.50	75.5	53.4 - 99.9	18.6	10.9 - 28.3
Cobalt ($Co(NO_3)_2$)	0.49	0.38 - 0.59	120	64.4 - 176	38.2	14.1 - 69.6
Arsenic ($NaAsO_2$)	0.55	0.49 - 0.61	134	104 - 164	42.1	28.6 - 57.4
Aluminum ($AlCl_3$)	0.56	0.51 - 0.61	369	301 - 420	260	190 - 315
Antimony ($SbCl_3$)	0.66	0.53 - 0.79	157	101 - 216	48.9	24.8 - 79.2
Molybdenum (Na_2MoO_4)	0.79	0.61 - 0.99	125	76.5 - 183	27.8	13.5 - 48.3
Zirconium ($ZrCl_4$)	1.08	0.70 - 1.57	79.0	32.2 - 150	10.3	2.4 - 24.1
Zinc ($ZnCl_2$)	1.12	1.00 - 1.24	451	366 - 533	216	157 - 275
Manganese ($MnCl_2$)	2.91	2.60 - 3.23	958	779 - 1134	388	280 - 501
Gallium ($GaCl_3$)	3.51	2.47 - 4.73	316	156 - 540	44.5	15.6 - 96.7
Tantalum ($KTaO_3$)	4.33	3.08 - 5.84	525	260 - 869	94.0	32.0 - 198
Selenium (Na_2SeO_4)	5.17	4.15 - 6.26	786	483 - 1137	169	79.9 - 296
Titanium ($TiCl_4$)	7.31	5.33 - 9.51	981	513 - 1578	191	72.7 - 381
Lithium ($LiCl$)	9.28	6.68 - 12.3	1783	901 - 2826	464	163 - 916
Tungsten (Na_2WO_4)	16.5	14.0 - 19.4	3651	2609 - 4748	1066	629 - 1591
Tellurium (K_2TeO_3)	21.6	14.5 - 30.6	1263	523 - 2377	125	31.5 - 327
Barium ($BaCl_2$)	42.7	32.2 - 54.2	9543	5566 - 14097	2813	1267 - 4924
Boron (H_3BO_3)	70.1	37.0 - 184	1016	156 - 2067	31.6	0.8 - 191
Cesium ($CsCl$)	181	133 - 235	21826	9807 - 37054	3887	1092 - 8842
Magnesium ($MgCl_2$)	1355	1199 - 1507	660500	517600 - 788000	367600	254800 - 475800

solid wastes at concentrations sufficient to pose appreciable risk to trout and other aquatic biota (Table 1).

Particular attention was given to exposure levels which produced 10% (LC_{10}) and 1% (LC_1) impairment of test populations, to evaluate use of such probit-derived values for (1) approximating threshold concentrations, and (2) application in initial hazard assessment programs. To determine reliability of the LC_1 values, they were compared with MATCs or no effect concentrations developed in continuous flow embryo-larval and chronic life-cycle tests, as well as with current freshwater criteria.[35] The LC_1 of 0.2 µg/l mercury was in close agreement with MATCs determined in chronic studies with the fathead minnow[21] (0.07-0.13 µg/l), flagfish[21] (0.17-0.33 µg/l), and brook trout[36] (0.29-0.93 µg/l), and with the freshwater criterion of 0.05 µg/l.[35] However, in continuous flow embryo-larval and chronic reproductive tests with the rainbow trout, developmental stages suffered lethality at 0.1 µg/l mercury.[22,32] Though data on silver were limited, the LC_1 of 0.1 µg/l agreed closely with a long term no effect concentration set between 0.09 and 0.17 µg/l in an 18-month study with the rainbow trout.[37] The copper LC_1 of 3.4 µg/l was close to estimated MATC ranges of 3.0 to 5.0 and 5.0 to 8.0 µg/l determined for the brook trout by Sauter et al.,[38] and just below the no effect concentration of 9.4 µg/l given by McKim and Benoit.[39]

The cadmium LC_1 of 8.0 µg/l was in agreement with estimated MATCs for eight species of fish,[21] including the range of 3.8 to 11.7 µg/l determined for brown trout.[40] An MATC of 1.7 to 3.4 µg/l was established for chronically exposed brook trout,[41] and present EPA criteria for salmonids were set at 0.4 and 1.2 µg/l for cadmium in soft and hard water, respectively.[35] The chromium LC_1 was 21.5 µg/l, compared to an estimated MATC of 51 to 105 µg/l established in a 60-day test with embryonic, larval, and juvenile stages of the rainbow trout.[38] In a complete life-cycle study with the brook trout, the MATC range for chromium was 200 to 350 µg/l,[42] and the EPA criterion for aquatic life was set at 100 µg/l.[35] In life-cycle studies with Daphnie magna, Biesinger and Christensen[43] reported 16% reproductive impairment at a chromium concentration of 330 µg/l, while Trabalka and Gehrs[44] observed significant effects on survival and reproduction at exposure levels as low as 10 µg/l.

In studies with lead, MATC ranges of 31.3 to 62.5 and 58 to 119 µg/l were determined in chronic reproductive tests on the flagfish[21] and brook trout,[45] respectively. An MATC for rainbow trout was estimated to fall between 71 and 146 µg/l in 60-day tests on developmental and juvenile stages.[38] However, the toxicity of lead may vary substantially depending on water hardness and other test conditions.[35,46] In chronic studies with the rainbow trout,[46] MATCs for total lead administered in soft water were within ranges of 4.1 to 7.6 µg/l and 7.2 to 14.6 µg/l, depending on whether exposure was initiated at the eyed stage or after hatching. The most sensitive test responses included discoloration of the tail and abnormalities of the spinal column (i.e., lordosis, scoliosis). These MATCs closely approximated the LC_1 of 10.3 µg/l given in Table 2. It is important to note that the latter value was determined by combining frequencies for embryo-larval lethality and teratogenesis, basing exposure on total lead administered in moderately hard water.

No chronic data were available for beryllium, but the LC_1 did not differ significantly from the EPA criterion of 11 µg/l established for aquatic life exposed in soft water.[35] The LC_1 for cobalt was 38.2 µg/l, and this was in reasonable agreement with an MATC of 48.7 to 112.5 µg/l, which we estimated from results on growth and survival obtained in 30-day tests with embryos and larvae of the fathead minnow.[47] In the latter investigation, the bioconcentration of cobalt was significant at 48.7 µg/l.

Though a final criterion for arsenic has not been developed, the EPA recommendation for domestic water supplies (50 µg/l) was considered adequate to protect aquatic life.[35] The arsenic LC_1 was 42.1 µg/l. Zinc gave an LC_1 of 216 µg/l, compared to MATCs of 30 to 180 and 532 to 1368 µg/l determined in chronic reproductive studies with the fathead minnow[48] and brook trout,[21] respectively. In addition, the LC_1 was in close agreement with the estimated MATC of 139 to 267 µg/l obtained in 30-day tests with the flagfish.[49] The boron LC_1 of 31.6 µg/l was obtained in tests conducted in moderately hard water (100 mg/l $CaCO_3$) and was approximately midrange between values reported in continuous flow tests in which trout embryos and larvae were exposed in soft and hard water.[30] Compared with a boron LC_{50} of 70.1 mg/l, the LC_1 was unusually low. However, this was due in large part to teratogenic effects of boron observed at low concentrations.[30] The LC_{10} of 1016 µg/l further characterized the gradual slope of the dose-response curve obtained for boron. Though chronic data were not available for magnesium, the LC_{50} of 1355 mg/l appeared reasonable in view of 96-hour LC_{50}s which ranged up to 4200 mg/l for adult fish.[50] In tests with magnesium, water hardness was substantially increased at the higher exposure levels.

A poor correlation between LC_1 and MATC values was observed for nickel. Despite the importance of nickel in hazard assessment programs for oil shale and coal, chronic toxicity tests with this element have been limited to very few aquatic species. The most comprehensive investigation was conducted on the fathead minnow by Pickering.[51] Nickel concentrations up to 1.6 mg/l did not affect survival or growth of the first generation of fish, which were 6 weeks of age at the onset of exposure. Spawning began after approximately 5 months, and both fecundity and egg hatchability were sharply reduced at a mean nickel concentration of 730 µg/l. The average number of eggs per spawning was 66 and hatchability was 42%, compared to control values of 188 and 94%, respectively. Though egg production appeared repressed at lower exposure levels, results could not be verified statistically. For example, when nickel was administered at 380, 180, and 82 µg/l, mean egg production per female for all spawnings was 13% to 31% less than observed for controls. The maximum acceptable toxicant concentration for nickel in hard water was judged to fall between 380 and 730 µg/l, and Pickering[51] predicted an MATC of 68 to 132 µg/l for fathead minnows exposed in soft water.

In other investigations, Biesinger and Christensen[43] reported 50% and 16% reproductive impairment in Daphnia at nickel concentrations of 95 and 30 µg/l, respectively. While Daphnia and the fathead minnow may differ in their tolerances to nickel,[35] the wide variation between results of Biesinger and Christensen[43] and Pickering[51] probably resulted in part from the different statistical procedures applied to their data. Biesinger and

Christensen obtained concentrations for reproductive impairment using the method of Litchfield and Wilcoxon,[52] which involved fitting a regression line to dose-response data plotted on logarithmic-probability paper.[53] On the other hand, Pickering applied analysis of variance to his results. Even though he used four replicates per treatment level and obtained good precision in regulating exposure concentrations of nickel, it was not possible to show significance for the consistent reductions in fecundity observed at all exposure levels below 730 μg/l. Time and cost limitations involved in long term investigations frequently curtail use of sufficient replicate exposures to provide adequate differentiation of low-level test responses using the more traditional statistical procedures (e.g., analysis of variance). Therefore, when the dose-response is adequately characterized, regression analysis generally provides a more effective means of approximating threshold concentrations for toxic effects.[24] When data obtained with trout embryo-larval stages were analyzed using log probit regression, sensitivity to nickel equalled or exceeded that observed for Daphnia (Table 2). The LC_{10} and LC_1 values were 10.6 and 3.0 μg/l. In other static renewal tests with embryos and larvae, nickel LC_1s of 3.6, 10.6, and 97.7 μg/l were obtained for the channel catfish, largemouth bass, and goldfish.[54] It should be noted that these values, as well as those presneted in Table 2, were determined with the probit method of Finney,[28] rather than by Daum's procedure[29] which was used in previous investigations. This, together with inclusion of some additional data from replicate experiments, gave lethal concentrations which differed slightly from preliminary findings.[3,26,32]

The data correlations reviewed above were complicated somewhat by differences in test procedures, water conditions, and animal test species. However, where data were sufficient to permit comparisons, LC_1s obtained in static renewal embryo-larval tests with trout were in reasonable agreement with no effect concentrations and MATCs determined in continuous flow embryo-larval and chronic life-cycle studies and with most existing EPA criteria for freshwater biota.[35] Differences between LC_1s and MATCs for specific elements generally were no greater than variations among MATCs reported in different investigations (Table 3). Also as shown in Table 3, an interesting relationship existed between LC_{10} values and metal concentrations which produced 16% reproductive impairment in Daphnia magna.[43] Compared with Daphnia on this basis, trout embryo-larval stages were more sensitive to As, Hg, Mn, Ni, Sn, and Sr, about equally affected by Al, Ba, Cu, and Pb, and more tolerant to Cd, Co, Mg, and Zn. When the different elements were compared for relative toxicity, the order varied somewhat depending on whether LC_{50}, LC_{10}, or LC_1 values were used (Table 2). The order of toxicity of metals to chronically exposed Daphnia also varied to some extent when determined by LC_{50}s. Maximum acceptable toxicant concentrations given in Table 3 were estimated from 30- to 90-day continuous flow embryo-larval tests or determined in partial and complete life-cycle studies, and the values for Daphnia were taken from Biesinger and Christensen.[43] The EPA Red Book[35] was the source for criteria for freshwater aquatic life, as revisions currently in progress were not available for inclusion in this study.

Table 3. MATC'S COMPARED WITH LC$_1$ AND LC$_{10}$ VALUES DETERMINED IN STATIC RENEWAL TESTS WITH TROUT EMBRYO-LARVAL STAGES

Element[1]	LC$_{10}$[2] (µg/l)	LC$_1$[2] (µg/l)	MATC[3] (µg/l)	Species	Test[4]	Daphnia[5] (µg/l)
Aluminum	369	260	-	-	-	320
Arsenic	134	42.1	-	-	-	520
Barium	9543	2813	-	-	-	5800
Cadmium	29.2	8.0	1.7 - 3.4	brook trout[41]	clc	0.17
			3.0 - 6.5	flagfish[21]	el	
			3.8 - 11.7	brown trout[40]	el	
			4.1 - 12.5	coho salmon[40]	el	
			7.4 - 16.9	flagfish[21]	clc	
			8.1 - 16.0	flagfish[49]	el	
Chromium	56.9	21.5	51 - 105	rainbow trout[38]	el	330
			200 - 350	brook trout[42]	clc	
Cobalt	120	38.2	-	-	-	10
Copper	16.5	3.4	3.0 - 5.0	brook trout[38]	el	22
			5.0 - 8.0	brook trout[38]	el	
			9.4 - 17.4	brook trout[39]	clc	
Lead	40.9	10.3	4.1 - 7.6	rainbow trout[46]	plc	30
			7.2 - 14.6	rainbow trout[46]	plc	
			31.3 - 62.5	flagfish[21]	clc	
			58 - 119	brook trout[45]	clc	
			71 - 146	rainbow trout[38]	el	
Magnesium	660500	367600	-	-	-	82000
Manganese	958	388	-	-	-	4100
Mercury	0.9	0.2	0.07 - 0.13	fathead minnow[21]	clc	3.4
			0.17 - 0.33	flagfish[21]	plc	
			0.29 - 0.93	brook trout[36]	clc	
Nickel	10.6	3.0	380 - 730	fathead minnow[51]	plc	30
Silver	0.9	0.1	0.09 - 0.17	rainbow trout[37]	plc	-
Strontium	49.0	13.0	-	-	-	42000
Tin	75.5	18.6	-	-	-	350
Zinc	451	216	30 - 180	fathead minnow[48]	plc	70
			139 - 267	flagfish[49]	el	
			532 - 1368	brook trout[21]	plc	

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[1] Administered in static renewal tests from fertilization through 4 days post-hatching.

[2] Determined with the probit method of Finney[28], rather than the procedure of Daum[29] used in earlier investigations[3,26,32].

[3] Additional values were presented by McKim[21].

[4] MATC's were estimated from 30 to 90-day embryo-larval tests (el) or determined in partial (plc) and complete (clc) life-cycle studies.

[5] Chronic values for 16% reproductive impairment given by Biesinger and Christensen[43].

Firm criteria for aquatic biota have been developed for only a small fraction of the elements which occur in process waters and solid wastes associated with oil shale and coal (Table 1), and energy engineers are faced with an uncertain future concerning regulatory guidelines for waste disposal. Consistent with recommendations of the Interagency Workshops on Oil Shale[55] and Coal Conversion,[25] early identification of potential hazards is essential to assure environmental acceptability of new and rapidly emerging energy technologies. The promulgation of freshwater criteria has progressed slowly since implementation of the Water Quality Act of 1965, due in substantial measure to the stringent requirements of the present testing program. Static renewal bioassays evaluated in the present investigation can be conducted at a small fraction of the time and cost involved in partial and complete chronic life-cycle tests generally used to establish MATCs for aquatic life. As rainbow trout are endemic to many waters which potentially may be affected by the processing of oil shale, the LC_1s and LC_{10}s given in Table 2 should be useful in estimating impact of contaminants on aquatic biota, pending development of regulatory criteria by State and Federal agencies. It should be noted, however, that toxicity of trace elements in antural waters may be affected by various transport-fate phenomena, water characteristics (e.g., pH, hardness, suspended solids), or chemical form and solubility of the contaminant.[35,56,57] The comparative toxicological ranking given in Table 2 should also be useful in prioritizing trace elements for more comprehensive studies on environmental monitoring and biological effects. Particular attention should be given to the more toxic elements which appear at appreciable concentrations in oil shale waste products (Table 1).

Trout embryo-larval tests also were conducted on simple metal mixtures, to evaluate possible antagonistic, additive, or synergistic interactions. Mercury was mixed in equal proportions with each of three other metals, and the resulting LC_{50}s (μg/l) with 95% confidence limits given parenthetically were 10 (6-18), 10 (9-12), and 18 (12-25) for mercury-cadmium, mercury-selenium, and mercury-copper, respectively. Given in the same order, LC_{50}s (μg/l) calculated for additive effects were 25 (19-32), 90 (64-131), and 15 (12-20). Except for mercury-copper, the actual LC_{50}s reflected net synergism. However, as noted in earlier studies,[22,26] analysis of dose-response data clearly indicated that the type of interaction varied with exposure concentration. The results for mercury-copper are shown in Figure 1. Antagonism was observed at 1 to 10 μg/l ($P < 0.005$). Throughout this exposure range, the hatchability of trout eggs consistently exceeded frequencies calculated for additive effects, but synergism became significantly at 50 μg/l ($P < 0.001$). Based on LC_{50} values given in Table 2, mercury was more than 20 times as toxic to trout eggs as copper. However, the mercury-copper mixture was less toxic than copper at lower exposure levels, but equally as toxic as mercury at high concentrations. Below median lethal concentrations, mercury-selenium and mercury-cadmium were moderately antagonistic to additive, and synergism was observed only at higher exposure levels. On the basis of these initial results, it appears that synergism usually is dependent on high exposure concentrations and, therefore, less likely to be a significant factor in most natural trout waters. This is consistent with earlier results of in situ embryo-larval tests conducted on coal ash effluents which contained complex metal mixtures.[3]

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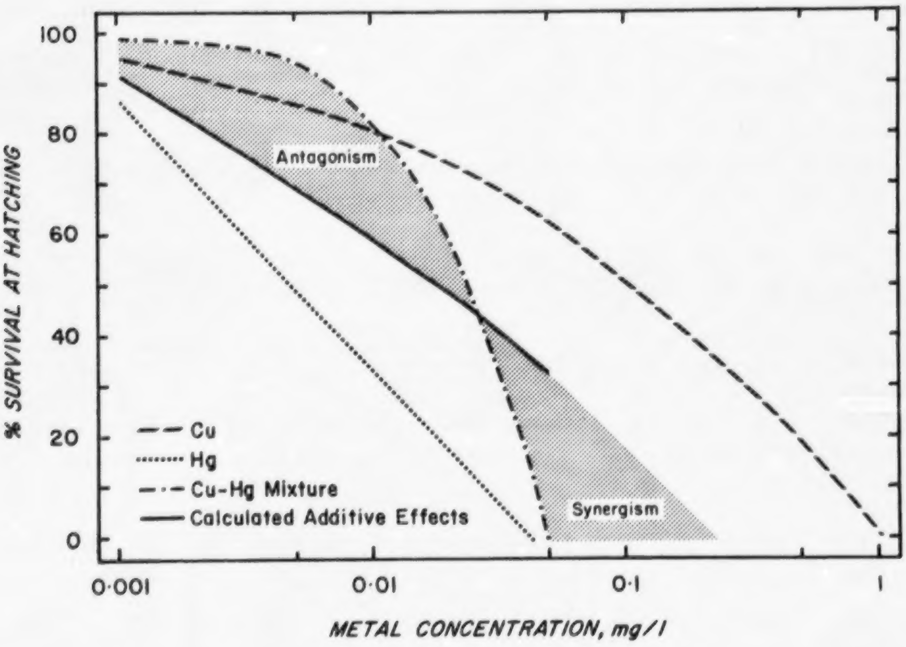

Figure 1. Effects of mercury-copper mixture on rainbow trout embryos. Mercury and copper were mixed in equal proportions and administered from fertilization through hatching (24 days).

AN ANALYTICAL METHOD FOR ASSESSING THE QUALITY, BY MICROBIAL EVALUATION, OF AQUEOUS EFFLUENTS OBTAINED FROM AN IN SITU OIL SHALE PROCESS*

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ABSTRACT

An analytical method was developed for the enumeration of microorganisms which grow in waste waters (retort water) derived from an *in situ* oil shale processing experiment (Laramie Energy Technology Center Rock Springs Site 9 Experiment, Omega-9 retort water). These waters are high in hydrocarbon components which may be inimical in the environment, but subject to degradation by microorganisms.

Growth of indigenous microbial populations occurred rapidly in the retort water. A culture medium was developed for the appraisal of microbial proliferation which was compared with, and found to be superior to, standard media for the enumeration of pollution indicators.

INTRODUCTION

Determining environmental interactions and fate of, and devising treatment and control systems for aqueous effluents derived from *in situ* oil shale processing are areas of active research (Farrier et al. 1978a; Farrier et al. 1978b).[1,2] Previous studies have shown that high aerobic and anaerobic heterotrophic bacterial population densities occur concomitantly with an increase in the turbidity of freshly filtered (0.4 μm) Omega-9 retort water after a few days incubation at room temperature (Farrier et al. 1977).[3] Proliferation of these microorganisms significantly alters the nature and concentrations of dissolved organic (Felix, Farrier and Poulson,

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1977; Pellizzari, 1978)[4,5] and inorganic (Fox, 1978)[6] constituents. Thus, microbial evaluation of effluents derived from in situ oil shale processing is warranted in order to completely characterize such waters. This paper presents the development of new microbial analytical methods suitable to these waters and compares such methods with standard procedures.

MATERIALS AND METHODS

Omega-9 Retort Water

The acquisition, processing and storage of Omega-9 retort water has been previously reported (Farrier et al., 1977)[3] Fox, Farrier and Poulson (1978); Farrier, Fox and Poulson (1979)[7,8] have detailed elemental and water quality analyses and Leenheer and Farrier (1978)[9] the qualitative organic analysis of the Omega-9 sample. All Omega-9 retort water described in this study was stored at 2±1C.

Preparation of Retort Water Agar (RWA)

Retort water samples for microbial evaluation were aseptically withdrawn from a 114 liter, polypropylene lined, storage drum in 1-1.5 liter aliquots as needed. The retort water was centrifuged (90 min, 5C, 5500 x G) to remove suspended materials and rendered aseptic by passing through three sterile membrane filters stacked in series (1.2, 0.45, 0.22 µm), under 0.68 atm (10 lb/in^2) N_2 pressure. Filter sterilization was repeated and flasks containing the retort water were placed on a rotary shaker (128 rpm) for 18-36 hour incubation at 20-25C. Flasks which became visually turbid (indicative of the presence of microorganisms) were presumed contaminated and discarded. Nitrogen (25 mM KNO_3), phosphorus (5 mM K_2HPO_4), calcium (5 mM $CaCl_2$), and magnesium (5 mM $MgCl_2 \cdot H_2O$) were added to water agar (3% W/V agar in deionized water) and sterilized by autoclaving. Equal volumes of autoclaved water agar (cooled to 50C) and filter-sterilized retort water (warmed to 50C) were mixed, resulting in a final agar concentration of 1.5%. The Retort Water Agar (RWA) was dispensed into sterile petri dishes. Addition of the nutrients was to obviate the possibility that insufficient quantities would limit microbial growth. Justification for addition of nutrients was predicated on our findings and that of other investigators (Ossio et al., 1978)[10] which showed increased growth with the addition of nitrogen, phosphorus, calcium and magnesium. The protocol detailing the handling and sterilization of Omega-9 is presented in Figures 1 and 2.

Evaluation of Microbial Growth Kinetics

An experiment was performed to assess the growth kinetics exhibited by indigenous Omega-9 retort water microorganisms. One liter of Omega-9 retort water was placed on a rotary shaker (128 rpm) and incubated at 22-25C. Microbial growth was measured spectrophotometrically (Beckman Model 25) at 660 nm by measuring the absorbance of three ml aliquots of retort water at two-hour intervals until a stationary growth phase was established. Absorbance in these aliquots was measured against a filter-sterilized retort water blank. The growth rate constant (Mandelstam and McQuillan, 1973)[11] and generation time (Stanier, Doudoroff and Adelberg, 1970)[12] were calculated.

Figure 1. PRE-STERILIZATION PREPARATIVE SCHEME FOR OMEGA-9 RETORT WATER

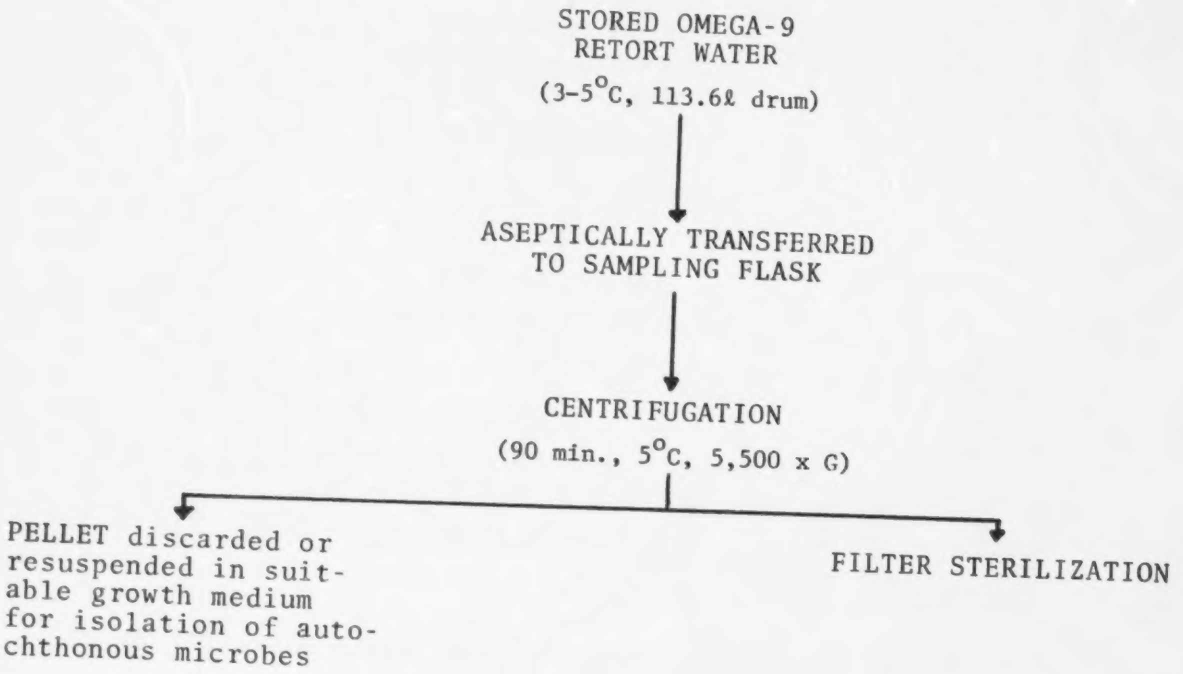
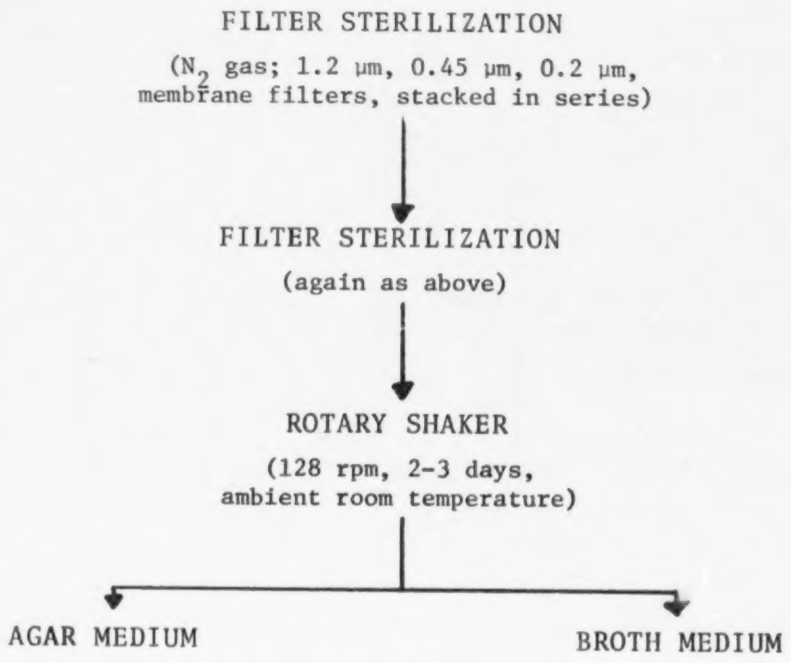

STORED OMEGA-9
RETORT WATER
(3-5°C, 113.6ℓ drum)
ASEPTICALLY TRANSFERRED
TO SAMPLING FLASK
CENTRIFUGATION
(90 min., 5°C, 5,500 x G)
PELLET discarded or resuspended in suitable growth medium for isolation of autochthonous microbes
FILTER STERILIZATION

Figure 2. FILTER STERILIZATION PROTOCOL FOR OMEGA-9 RETORT WATER


FILTER STERILIZATION
(N_2 gas; 1.2 µm, 0.45 µm, 0.2 µm, membrane filters, stacked in series)
FILTER STERILIZATION
(again as above)
ROTARY SHAKER
(128 rpm, 2-3 days, ambient room temperature)
AGAR MEDIUM
BROTH MEDIUM

Evaluation of Standard Media for the Enumeration of Retort Water Microorganisms

Standard methods for evaluating microorganisms in domestic and recreational waters involve the appraisal of total and fecal coliforms, fecal streptococci and total viable microbial populations. Coliforms and fecal streptococci bacteria were enumerated from sewage effluent and a turbid retort water culture by standard membrane filtration procedures (APHA, 1975).[13] Microorganisms in these inocula were also counted on Plate Count Agar, PCA, Modified Henrici Agar, Ha (Stark and McCoy, 1938)[14] and RWA. PCA is the standard recommended medium for total population counts (APHA, 1975).[13] HA has been shown to be superior to PCA in the enumeration of bacterial populations derived from alpine water sources (Skinner et al., 1974a; Skinner et al., 1974b).[15,16]

Control plates of all media were inoculated with filter-sterilized retort water to obviate the possibility that components in the Omega-9 process water might interfere with the indicator systems of the standard media (i.e., MFC broth for fecal coliforms, M-Endo broth for total coliforms and KF agar for fecal streptococci).

Sewage effluent was obtained from the last in a series of three lagoons which constitute the Laramie, Wyoming sewage treatment system. A one liter sample was aseptically colleted. One- and ten-ml volumes of sewage effluent were eluted through sterile Millipore HC 0.45 μm membrane filters and plated on the standard media. These filters are efficacious for cultivating microorganisms on their surface (Green, Clausen and Litsky, 1975).[17] The sewage sample was plated in duplicate on PCA, HA and RWA. One hundred ml aliquots of turbid retort water culture were eluted through sterile HC filters and plated in duplicate on the various standard media. This inoculum was also plated in duplicate on PCA, HA, and RWA. All PCA, HA and RWA plates were incubated for one week at 20C. This temperature was chosen to obviate the possibility that some microbes (e.g., facultative psychrophiles) would be excluded if the standard 35C incubation temperature was used. The experimental design is depicted in Figure 3.

RESULTS

Evaluation of Microbial Growth Kinetics

The growth curve (Figure 4) illustrates the kinetics of microbial growth by autochthonous retort water microorganisms. The exponential growth phase began after four hours incubation and lasted ten hours, at which point the organisms entered stationary growth phase. A generation time of 110.6 minutes (growth rate constant of 0.376) was computed for the exponential growth period.

Evaluation of the Growth of Microorganisms on Selected Media

The results of the study evaluating growth of microorganisms on standard media (Figure 5) suggest that standard indicator systems are, indeed,

Figure 3. DESIGN OF EXPERIMENT COMPARING MEDIA FOR STANDARD EXAMINATION OF WASTE WATER AND RETORT WATER.

	ENUMERATION METHOD					
	MEMBRANE FILTRATION PROCEDURE			STANDARD PLATE COUNT PROCEDURE		
POPULATION AND MEDIUM / INOCULUM	FECAL COLIFORMS (MFC)	TOTAL COLIFORMS (M-ENDO)	FECAL STREPTOCOCCI (KF AGAR)	TOTAL COUNT (PCA)	TOTAL COUNT (HA)	TOTAL COUNT (RWA)
LARAMIE SEWAGE EFFLUENT	○	○	○	○	○	○
TURBID OMEGA-9 RW	○	○	○	○	○	○
FILTER-STERILIZED OMEGA-9 RW	○	○	○	○	○	○

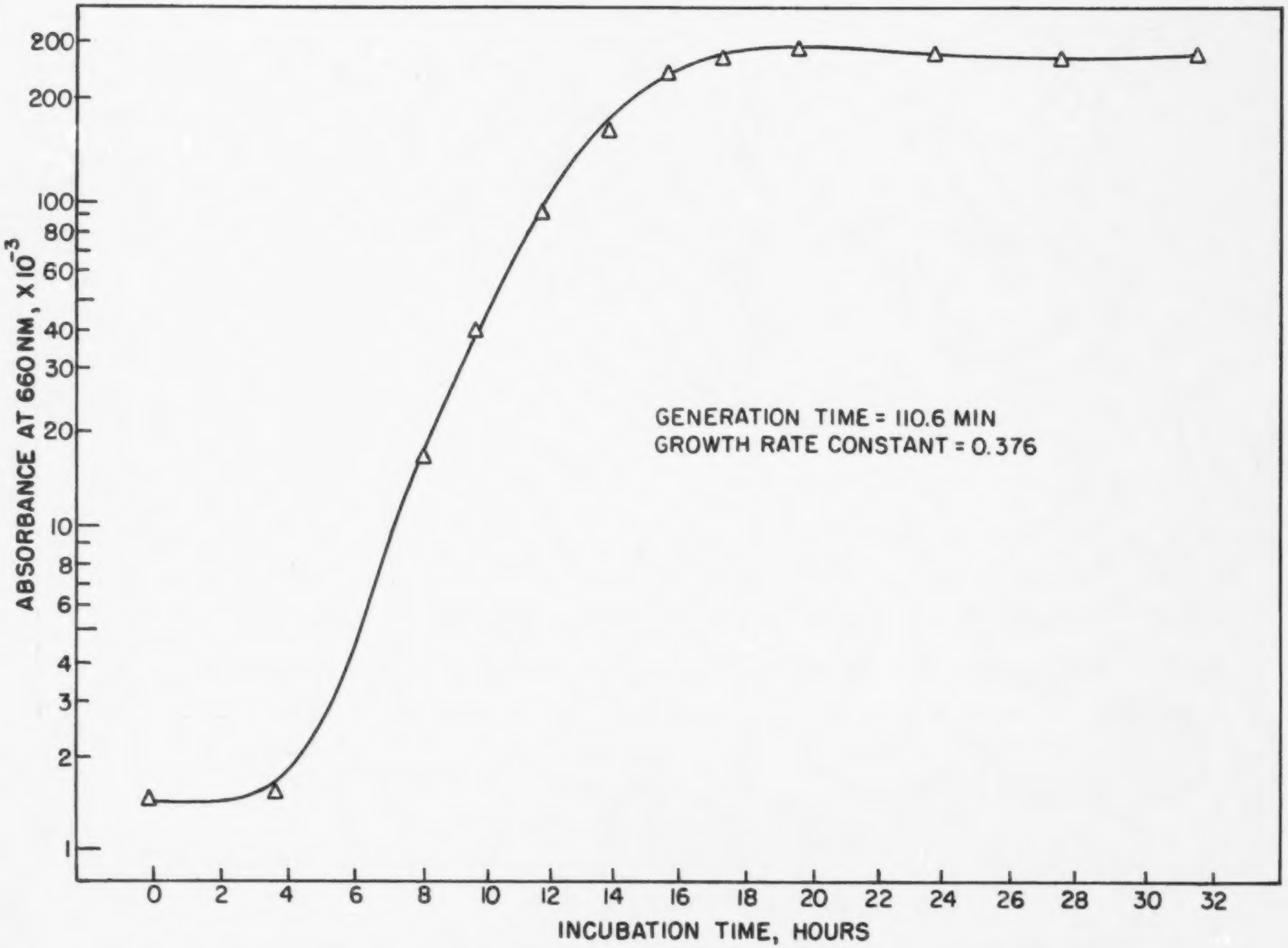


Figure 4. GROWTH CURVE OF AUTOCHTHONOUS MICROORGANISMS IN RETORT WATER. ABSORBANCE IS DIRECTLY PROPORTIONAL TO MG DRY WEIGHT OF MICROORGANISMS.

Figure 5. COMPARISON OF MEDIA FOR STANDARD EXAMINATION OF WASTE WATER AND RETORT WATER.

POPULATION AND MEDIUM / INOCULUM	MICROORGANISMS/100 ml					
	MEMBRANE FILTRATION PROCEDURE			STANDARD PLATE COUNT PROCEDURE		
	FECAL COLIFORMS (MFC)	TOTAL COLIFORMS (M-ENDO)	FECAL STREPTOCOCCI (KF AGAR)	TOTAL COUNT (PCA)	TOTAL COUNT (HA)	TOTAL COUNT (RWA)
LARAMIE SEWAGE EFFLUENT	5.4×10^3	1.8×10^4	2.6×10^4	2.1×10^8	1.3×10^9	1.1×10^3
TURBID OMEGA-9 RW	0	0	0	1.4×10^9	2.4×10^9	5.3×10^9
FILTER-STERILE OMEGA-9 RW	0	0	0	0	0	0

appropriate for counting microorganisms in sewage effluent. Conversely, bacteria native to retort water do not grow on coliform or streptococci enumeration media. HA was approximately sixfold better than PCA in evaluating total heterotrophic populations from the sewage inoculum. This corroborates the findings of Skinner et al.,[15,16] who compared these media in alpine waters (1974a, 1974b). By comparison, RWA was not adequate for enumerating microorganisms from sewage sources. PCA and HA are approximately equal for counting retort water microorganisms; whereas, RWA is three to four times better than PCA or HA in culturing retort water microbes. Retort water did not affect the indicator systems in the standard media.

DISCUSSION AND CONCLUSIONS

Conclusions from this study can be summarized as follows:

1. Growth of microorganisms in Omega-9 retort water is rapid.
2. Sewage microorganisms do not grow substantially on retort water agar.
3. Standard media for the enumeration of bacteria from domestic and recreational water sources do not support the growth of microorganisms derived from Omega-9 retort water.
4. Autochthonous retort water microorganisms grow well on a medium containing Omega-9 retort water as the only source of carbon and energy.

The kinetics of microbial growth study provided evidence that native microorganisms are capable of rapid growth in the process water. One can infer that the original constituents of the retort water are being altered as the result of microbial growth since the water provided the sole carbon and energy sources. Current studies are assessing this hypothesis.

Based on the results of experimentation set forth above, one might be prompted to question why standard analyses should be considered at all in the analysis of oil shale waste waters. As pointed out in a recent article in Environmental Science and Technology (Miller, 1978),[18] a goal of the Environmental Protection Agency's Quality Assurance program is the standardization of analytical procedures for water quality. Where this is conceptually a practical approach to quality assurance, it might not immediately be feasible for oil shale process waters or domestic sources contaminated with oil shale waste effluent. Where microbial populations are concerned, methodologies for assessment of water quality should detail a specific group or type of pollutant especially where rapid microbial growth has been demonstrated, as in this study. The standard indicators, fecal coliforms and fecal streptococci, appear to be adequate for evaluating fecal pollution. One would not expect to find these indicators in oil shale waste waters, but the necessity to look for them may be required in waters where there has been an admixture of oil shale waste effluent with domestic or recreational sources. Total heterotrophic bacteria enumerated on PCA might provide data which are indicative of changes in total populations with time, but fail to reflect potential population shifts; e.g., from an environmentally diverse population to one selected for by the type of pollutant. If retort water comes into contact with soil or other waters, its presence may selectively enrich microorganisms that can grow in it, thereby excluding other microorganisms whose role in nature might be uniquely important. The RWA medium constitutes an analytical method for evaluating such effects on microbial populations when coupled with PCA or HA.

The Omega-9 retort water used in this study may not be representative of retort waters in general. However, the medium described here could be prepared using any type of retort water. Therefore, we report a method which can be used to assess the microbiological quality of oil shale waste waters or sources contaminated with these effluents.

ACKNOWLEDGEMENTS

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MONITORING OF RETORTED OIL SHALE EFFECTS ON SURFACE SOIL NITROGEN FIXATION PROCESSES: A RESOURCE FOR DESIGN AND MANAGEMENT OF LAND RECLAMATION PROGRAMS

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ABSTRACT

Nitrogen fixation, both by free-living soil microbes and by *legume-Rhizobium* type associations, has been found to be particularly sensitive to material in retorted shales or in aqueous shale leachates, in comparison with other more general measurements of microbiological activity. With the important role which nitrogen fixation might play in the development of resources requiring revegetation and rehabilitation programs, the measurement of shale component effects on this process would appear to represent a convenient, inexpensive means of monitoring biological effects of oil shale residues during both the design and conduct of rehabilitation projects. To allow the most efficient utilization of this approach in the deisgn and monitoring of an oil shale rehabilitation project, quality assurance factors (QA) which should be considered, including site selection and sampling, measurement techniques, and interpretation considerations are discussed. With the relatively simplicity of these procedures, which have been used in a wide range of environmental applications, it is suggested that site selection and sampling are points where greater care should be given, to assure maximum usefulness of this parameter in relation to QA concerns.

INTRODUCTION

The importance of establishing and maintaining a functional microbiological community in a plant-soil system has been well documented (Alexander[1] Aspiras et al.[2]; Baver, Gardner and Gardner,[3] Harris et al.[4]), and these processes become especially important when establishing plant growth on raw or retorted oil shale materials. An important characteristic of retorted oil shale materials is the large amount of leaching which is required to allow plant growth (Harbert and Berg,[5] Ward, Marghiem and Löf[6]), and the range of potentially inhibitory materials which are present Schmehl[7] and McCaslin,[6] Shendrikar and Faudel[8]). With the potential to restabilize extensive areas which may be used for disposal of raw shale or retorted shale, even with *in situ* or especially with modified *in situ* processing, where a volume of shale equal to that of 25% of the volume processed may have to be disposed of on the surface, the need to monitor and design reclamation systems to minimize the potential effects of these materials or their leachates on plant-soil systems will be important.

As an additional aspect of this work, the production of large volumes of water in the retorting process makes it possible that these process materials may enter existing aquifers, and eventually mix with surface waters in particular geological situations. In this regard, biological nitrogen fixation has been found to be particularly sensitive to the presence of retorted shale (Hersman and Klein[9] [10]) and retorted shale leachates (unpublished data). The best known of these relationships is the one between legumes and bacteria of the genus Rhizobium. In addition to these plant-associated nitrogen fixing relationships, there are a number of free-living bacteria which fix nitrogen, including the cyanobacteria, and the genera Clostridium, Klebsiella, and Azotobacter (Brill[11]). The use of acetylene reduction as a means of assessing nitrogen fixation potential is widely used and accepted (Hardy et al.;[12] Hardy, Burns and Holsten,[13] Kapustka and Rice[14]). In our experiments, we have been investigating the effects of retorted oil shale additions on the nitrogen fixation potential of a Western Colorado surface soil collected from the Piceance Basin of Colorado. In addition, the effects of shale extracts on nitrogen fixation by a free-living Rhizobium species have been evaluated to detect possible changes in plant-associated nitrogen fixation which might be useful in a field monitoring program, where leachate characterization and control would be essential.

MATERIALS AND METHODS

Soils. All soils were derived from the intensive study area in the Piceance Basin area, and samples were sieved with a 2 mm mesh screen, mixed in a Patterson-kelly twin steel dry blender (Patterson-Kelly Co., East Stroudsburg, PA), returned to individual plastic bags, and stored at 6°C until used.

Retorted oil shale samples were taken from materials used to build soil-oil shale plant growth testing panels at the intensive study area. The retorted shale was produced by the Paraho process at Anvil Points, Colorado by Development Engineering Inc. Nitrogen fixation potential measurements for these soil samples were carried out using procedures described by Hardy, Burns and Holsten.[13] Specific equipment used in the laboratory included a gas chromatograph (Varian Aerograph; Walnut Creek, California) and an integrater recorder (Omniscribe Recorder, Houston Instrument Co., Austin, Texas) to allow calculation of peak areas. Acetylene and ethylene standards were obtained from the Applied Science Laboratories, State College, Pennsylvania. The separation of acetylene from ethylene was carried out using a 3-mm diameter x 183-cm length stainless steel column filled with Poropak Q (Waters Associates, Milford, Massachusetts), with a column bath temperature of 70°C.

Ten grams of soil were placed in serum bottles and brought to 60 percent of moisture holding capacity with a solution of 0.5 percent (w/v) glucose in water. The bottles were sealed with serum caps and flushed with

N_2 gas for 5 minutes. Then using a 5 ml syringe, 5 ml of gas from each bottle was replaced with 5 ml of acetylene. The bottles were incubated in the dark for 48 hours at 25°C. Using a 1 ml syringe, 1 ml of gas was withdrawn and injected into the chromatograph. Nitrogen fixation was expressed as nanomoles of ethylene produced per g soil^{1} · 48 hours^{1}.

The surface soil was mixed with either ethylene chloride extracted retorted oil shale, retorted oil shale, or sterile glass beads in a Patterson-Kelly dry soil blender to give control soils and mixtures of oil shale and soil at 10, 20, 30, and 40% by weight of added shale, or with an equivalent volume of glass beads as controls.

Rhizobium was grown in pure culture under conditions where nitrogen could be fixed, using procedures described by Keister,[15] Keister and Evans,[16] Kurz and LaRue,[17] and Pagan et al.[18] Shale was extracted using distilled water in a 2-1 ratio with retorted shale, and the leachate was separated by centrifugation after 3 hours of shaken incubation at 22°C. The leachate or retorted shale was added directly to a 24-hour culture of the active nitrogen-fixing *Rhizobium*, and monitored for relative acetylene reduction rates in comparison with control cultures.

RESULTS

Nitrogen fixation by organisms of the free-living *Azotobacter* type was found to be especially sensitive to the presence of retorted shale, and this effect was not simply due to the dilution of the soil with the shale materials, as the effects were distinctly greater than when soils were diluted with equivalent volumes of glass beads (Figure 1). Similar N_2 fixation responses were observed with normal and extracted shales, both of which were markedly different from the glass bead mixtures or the plain soil controls. The data suggest that retorted oil shale and retorted oil shale extracted with ethylene chloride contained substances inhibitory to the asymbiotic nitrogen fixing process, and that the observed reductions cannot be attributed to a dilution effect, since the responses of the shale mixtures at the higher shale concentrations were much lower than that for similar concentrations of glass beads.

In studies of retorted shale and retorted oil shale aqueous extract effects on nitrogen fixation by *Rhizobium* 32H1, similar distinct effects were observed (Figure 2). It is of interest to note that with the addition of the lower levels of retorted shale extract, that stimulation of nitrogen fixation occurred, which also has been noted to occur under specific test conditions using intact legume nodules (Hersman and Molitoris[19]). In these particular *Rhizobium* studies, the pH of the microbial suspensions did not vary more than 0.1-0.2 unit with the various additions, making it unlikely that these effects were due only to changes in the pH of the test systems.

DISCUSSION

Nitrogen fixation by soil microorganisms appears to be sensitive to the presence of retorted shale and shale leachates, and this procedure may

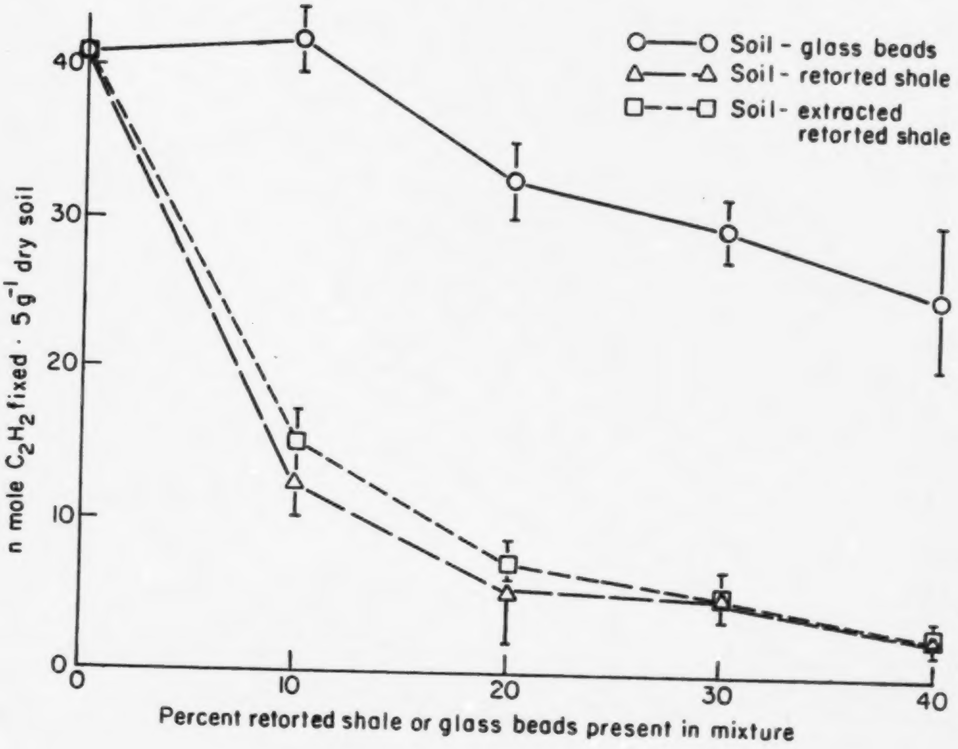

Figure 1. Ethylene production in soil-retorted oil shale, soil-extracted retorted shale, and soil-glass bead mixtures. Standard deviations are shown.

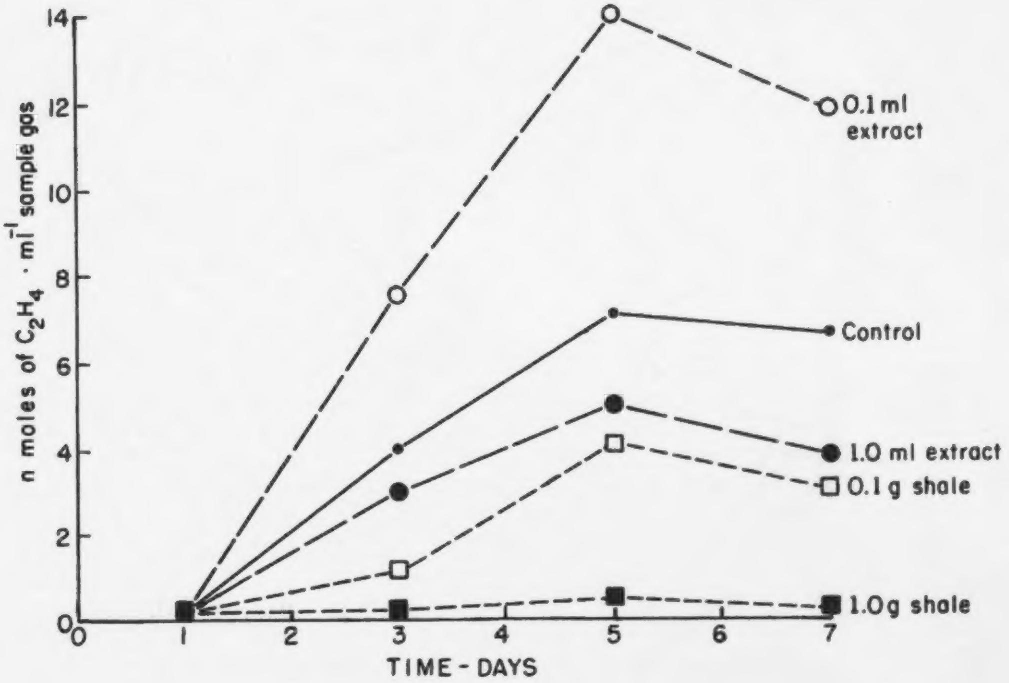

Figure 2. Retorted shale extract affects on acetylene reduction by Rhizobium 32H1 cultivated in the absence of a host plant.

provide a useful technique for monitoring the potential effects of these materials, and to assist in the design and monitoring of reclamation programs.

This approach to effects monitoring could be applied to provide the following information:

- To monitor the biological effects of different retorting processes under controlled laboratory conditions, at a minimum cost. This could be used to evaluate the relative effects of varied processing conditions on an easily measured biological process, and provide a means of developing correlations with chemical analysis information.
- To determine the effects of leachate movement through a compacted bed of retorted (or raw) oil shale during the testing and design phases for a particular stabilization program. This could be used to predict effects, especially when a possibility might exist of having water movement through a particular shale system. This would be especially critical in the design of capillary barriers which might be required to separate surface soil from a large volume of retorted shale.
- In areas where poor plant growth might occur after establishment of vegetative cover, the soils across a plant response gradient could be assayed for nitrogen fixation potential (in comparison with other biological and chemical measurements). Based on this type of information, corrective measures might be recommended, including additional barriers against moisutre movement, or the placement of additional soil to isolate leachate influenced materials.

In the use of this type of monitoring approach, the quality assurance (QA) considerations which have been discussed in a recent report in Environmental Science and Technology[20] should be considered; included the following:

- Site selection error
- Sampling error
- Measurement and reference sample error
- Data handling errors

For the use of a nitrogen fixation potential leachate toxicity assay under laboratory test conditions, site and sampling error effects should be able to be minimized, especially if 5-10 aliquots of 0.5-1.0 ml might be able to be taken from a particular leachate sample.

As the assays will be run at varied times and under different test conditions, it will be necessary to compare relative changes in nitrogen fixation rates under controlled conditions where the culture age, cell density and physiological condtions could be duplicated. An approach which could be used to minimize within sample variability would be to freeze leachate samples, and then to analyze the effects of a larger number of these samples, perhaps taken over a series of times, or from a range of locations simultaneously in the laboratory. To do this, it would be necessary to establish that freezing did not have specific effects on the antimicrobial characteristics of soil samples, shales or leachates.

As noted by Hardy et al.,[12] and Hardy, Burns and Holsten,[13] the measuring and reference sample error problems can be managed, based on the extensive prior use of this technique, and the ease of standardizing this analytical procedure.

Field sampling of soils will be more critical, especially with plant material established on particular sites. Sampling, soil mixing and statistical replication problems should be considered, and procedures which can be used for designing a sampling strategy have been described by Parkinson, Grey and Williams.[21] It is essential that time be minimized as a function in such sampling, as abiotic and biotic changes can occur at particular sites which might mask the effects of leachates on these nitrogen fixation processes. In a similar manner, through even minor changes in soil water content at particular sites, the rates of nitrogen fixation might be markedly influenced, making it difficult to analyze and interpret data.

If proper consideration of QA is given in the use of this technique, it would appear that this will provide information useful for better management of environments which are disturbed by oil shale processing.

ACKNOWLEDGMENTS

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THE EFFECTS OF SOIL PHOSPHORUS ON GROWTH AND ENDOMYCORRHIZAL DEVELOPMENT IN PLANT SPECIES NATIVE TO COLORADO'S OIL SHALE REGION*

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ABSTRACT

Two grass species and three shrub species native to the oil shale region of western Colorado were evaluated in terms of mycorrhizal infection, phosphorus content and growth. These results were correlated with levels of soil phosphorus available for plant use. Mycorrhizal infection appears to be dependent upon three factors (i.e., species, time, and plant-available soil phosphorus). Whereas most species become mycorrhizal very early when soil phosphorus levels are low and will eventually develop moderately heavy infections even when soil phosphorus levels are high, certain traditionally nonmycorrhizal species may become infected only under specialized conditions. Growth responses to mycorrhizal infection differ from species to species, but it is postulated that endomycorrhizal fungi benefit plant growth and survival in at least some species when phosphorus is a limiting factor. Reclamation programs on oil shale lands may be benefited by inoculation with certain species of mycorrhizal fungi.

INTRODUCTION

In light of the latest foreign oil supply crisis, our need for domestic oil sources will undoubtedly necessitate the utilization of shale oil at some future date. Disturbances accompanying kerogen retrieval and subsequent reclamation--rehabilitation efforts have generated at considerable amount of concern in many sectors. Integrated studies aimed at identifying rehabilitation potentials of areas rich in oil shale are presently being conducted by a group of researchers based at Colorado State University. An area located between the C-a and C-b oil shale tracts in the Piceance Basin of western Colorado has been designated as an "intensive study site," with a variety of fertility and disturbance studies being carried out by researchers from several disciplines.

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The microbiological components of belowground ecosystems are among the least studied and most poorly understood aspects of land rehabilitation and it is with the role these organisms play in ecosystem stability that the present study was concerned. A knowledge of these organisms appears to be a prerequisite to accurate assessment of rehabilitation potentials.

Among the microorganisms which have drawn the most attention and have been shown to be the most important in terms of plant growth, are a group of fungal symbionts known as mycorrhizal fungi. A mycorrhiza is a two-membered association consisting of root tissue and a specialized fungus. The relationship is mutually beneficial with the plant supplying carbohydrates to the fungus and the fungus aiding the plant in the uptake of mineral nutrients --primarily phosphate (P). It has also been suggested that mycorrhizae may reduce moisture stress in plants (Safir, Boyer and Gerdemann[1]).

Two types of mycorrhizal associations have traditionally been recognized. These are the ecto- and endotrophic forms. The fungal component of an ectomycorrhiza forms a mantle around the exterior of the root. Hyphae penetrate only into spaces between individual plant cells. These mycorrhizae are common in the family Pinacaea.

Endomycorrhizal fungi do penetrate the cortical cells of the host. A loose hyphal net extends into the soil surrounding the root but no mantle is formed. Most angiosperms have endomycorrhizal associations of the vesicular-arbuscular type, although certain families have traditionally been found to be nonmycorrhizal. The term vesicular-arbuscular mycorrhiza refers to fungal structures occurring within the cortex of infected roots. Vesicles are primarily fungal storage organs whereas arbuscules are sites of nutrient exchange. Chlamydospores are formed extracellularly and are a means of asexual reprodution.

Moorman and Reeves[2] have shown that reductions in VA endosymbiont populations are correlated with certain land disturbances. It has been suggested that nonmycorrhizal species may colonize disturbed areas due to lack of mycorrhizal inoculum and that this lack of inoculum may profoundly affect the stability of plant communities established by reclamation programs (Reeves, Wagner, Moorman and Kiel[3]). Reclamation of disturbed lands may be enhanced by the presence of mycorrhizal associations of both the ectotrophic and endotrophic type (Daft and Nicolson;[4] Daft, Hacskaylo and Nicolson;[5] Marx[6]).

A greenhouse growth study was undertaken in order to evaluate the effect of a native fungal endosymbiont (Glomus fasciculatus) on the growth of several plant species native to the Piceance Basin. Since phosphorus (P) and mycorrhizae appear to be so intimately linked (Gerdemann;[7] Nicolson;[8] Mosse[9]), it was determined that each species should be given varying amounts of phosphorus in both the mycorrhizal (M+) and nonmycorrhizal (M-) treatments. Figure 1 shows the experimental design of the study. Two shrubs species, Atriplex canescens (fourwing saltbush) and Eurotia lanata (winterfat) are members of the Chenopodiaceae which has traditionally been designated as a nonmycorrhizal family (Gerdemann[7]). Recently, however, several chenopods have been found to be infected with mycorrhizal fungi (Williams, Wollum and Aldon;[10] Aldon;[11] Williams and Aldon;[12] Reeves et al.[3]). For this reason, and because of conflicting reports on the effect and incidence of mycorrhizal infection in chenopods, the decision was made to use Atriplex and Eurotia in this growth study. Artemisia tridentata (big sage) was chosen because it is the dominant shrub throughout much of the Piceance Basin. The two grass species, Stipa viridula (green needlegrass) and Agropyron smithii (western wheatgrass) were chosen because they are common at the study site.

METHODS

Topsoil was obtained from an undisturbed area of the "intensive study site" previously mentioned. All soil was steamed for 20 hours, air dried and then reinoculated with washings of saprobic soil microorganisms isolated from Piceance Basin soil. The purpose of this was to parallel natural soil conditions as closely as possible, with the exception of the mycorrhizal element. Soil analysis results are shown in Table 1.

TABLE 1. RESULTS OF SOIL ANALYSIS

pH	8.2	NO_3-N	ppm	3.0
E.C.	1.0	P	ppm	9.0
Lime	High	K	ppm	212.0
% O.M.	2.6	Zn	ppm	1.7
SAR	0.3	Fe	ppm	6.8

No phosphorus was added to the soil of the low phosphorus regime. Monocalcium phosphate was used as fertilizer and was applied at the rates of 56 kg/ha or 25 ppm phosphorus in the medium phosphorus regime and 112 kg/ha or 50 ppm phosphorus in the high phsophorus regime (Figure 1).

Two kg of soil were measured into each pot. Two and one half g of corn roots heavily infected with Glomus fasciculatus, an endomycorrhizal fungas, were added to the mycorrhizal (M+) treatments as inoculum. Pots were seeded and watered to field capacity each day throughout the experiment. Pots were randomized on greenhouse benches and were rotated periodically. Half of the grasses were harvested at 90 days. The remaining grasses and the shrubs were harvested at 180 days. Height was measured on shrubs only. Tops were clipped just above the soil surface, oven dried at 75°C for 48 hours and weighed immediately on being taken from the oven. Roots from each pot were extracted from the soil, fixed in formyl acetic acid (FAA) and kept separately until they could be stained. One hundred 1 cm root sections randomly taken from each pot were stained in lactophenol-trypan blue (Phillips and Hayman[13]) and assessed for infection. Phycomycetous hyphae and either pelatons, arbuscules or vesicles were the criteria used for determining whether or not a root section was mycorrhizal.

	M+		M−	
no P	*Atriplex canescens*	7 reps	*Atriplex canescens*	7 reps
	Eurotia lanata	6 reps	*Eurotia lanata*	6 reps
	Artemisia tridentata	8 reps	*Artemisia tridentata*	8 reps
	Stipa viridula	9 reps	*Stipa viridula*	9 reps
	Agropyron smithii	9 reps	*Agropyron smithii*	9 reps
25 ppm P	*Atriplex canescens*	7 reps	*Atriplex canescens*	7 reps
	Eurotia lanata	6 reps	*Eurotia lanata*	6 reps
	Artemisia tridentata	8 reps	*Artemisia tridentata*	8 reps
	Stipa viridula	9 reps	*Stipa viridula*	9 reps
	Agropyron smithii	9 reps	*Agropyron smithii*	9 reps
50 ppm P	*Atriplex canescens*	7 reps	*Atriplex canescens*	7 reps
	Eurotia lanata	6 reps	*Eurotia lanata*	6 reps
	Artemisia tridentata	8 reps	*Artemisia tridentata*	8 reps
	Stipa viridula	9 reps	*Stipa viridula*	9 reps
	Agropyron smithii	9 reps	*Agropyron smithii*	9 reps

Figure 1. Experimental design of endomycorrhizal growth study.

The plant tops of species found to be mycorrhizal were assessed for phosphorus content. A perchloric acid digestion was performed on 1 gram samples of the dried plant material (Olsen and Dean[14]) and colorimetric determiantion of phosphorus was done by means of the vanadomolybophosphoric yellow color method (Jackson[15]).

RESULTS

Although winterfat and fourwing were inoculated in exactly the same manner as the other three species which developed extensive infections, neither of these chenopods became mycorrhizal. Since no infection was found to be present, a one-way analysis of variance was run on the height and weight data from these two species to determine whether or not the addition of phosphate fertilizer had an effect on their growth. The only significant difference found was a decrease in dry weight of winterfat in the high phosphorus regime (Table 2).

TABLE 2. WEIGHT AND HEIGHT DATA OF NONMYCORRHIZAL FOURWING SALTBUSH (A. CANESCENS) AND WINTERFAT (E. LANATA) GROWN UNDER CONDITIONS OF VARYING SOIL PHOSPHATE LEVELS*

	Atriplex Canescens		Eurotia Lanata	
	Weight (g)	Height (cm)	Weight (g)	Height (cm)
NO P	14.35a	59.7a	4.41a	61.4a
25 ppm P	13.73a	64.1a	4.57a	65.2a
50 ppm P	12.83a	58.9a	2.22b	44.9a

*Values are means of 7 replicates (*A. canescens*) and 6 replicates (*E. lanata*). Means in the same column followed by the same letters are not significantly different at the 0.05 level of probability.

In contrast to winterfat and fourwing saltbush, the M+ treatments of the grasses became heavily infected with mycorrhizal fungi. At both 90 and 180 days, infection levels in green needlegrass were greatly inhibited by both the medium and high phosphate fertilization rates (Table 3). This inhibition of mycorrhizal infection, apparently due to increased soil phosphorus concentrations, occurred consistently throughout the experiment. There were no significant differences in weight among any of the treatments. At 90 days there was actually a 24 percent increase in the M+, no phosphorus treatment over the M-, no phosphorus treatment. This increase was not, however, significant at the 5 percent level and was greatly minimized at 180 days. Close observation of the plants revealed that leaves of mycorrhizal plants were somewhat more succulent. This was true of western wheatgrass and big sage as well.

TABLE 3. THE EFFECTS OF PHOSPHATE FERTILIZATION ON SHOOT DRY WEIGHT, P CONCENTRATION AND ROOT INFECTION LEVELS IN GREEN NEEDLEGRASS (*S. viridula*)*

	Weight (g)		% Infection		µg P/g Plant Matter	
	90 days	180 days	90 days	180 days	90 days	180 days
M+ No P	4.57a	8.88a	61.8c	67.5d	12.0a	7.3a
M- No P	3.69a	8.31a	0.0a	0.0a	10.9a	6.8a
M+ 25 ppm P	4.44a	8.55a	20.0b	49.5b	14.0c	8.6a
M- 25 ppm P	3.87a	8.37a	0.0a	0.0a	13.8bc	9.0a
M+ 50 ppm P	4.31a	8.04a	8.8ab	54.0c	15.4c	8.8a
M- 50 ppm P	3.84a	7.42a	0.0a	0.0a	18.1d	9.0a

*Values are means of 5 replicates (90 days) and 4 replicates (180 days). Means in the same column followed by at least one of the same letters are not significantly different at the 0.05 level of probability.

Infection levels in western wheatgrass exhibited the same trends as seen in green needlegrass, with infection being inhibited by the addition of phosphate fertilizer. At 90 days the M+, no phosphorus treatment exhibited a 35 percent increase over the M-, no phosphorus treatment. This treatment was also significantly greater than the medium phosphorus M+ and M- treatments. At 180 days, however, there were no significant differences between those treatments (Table 4).

The analysis of plant material for phosphorus revealed that the presence of mycorrhizae neither increased nor decreased the amount of phosphorus in the plants (Tables 3 and 4). The results were quite consistent for both grasses. Generally, an increase in µg phosphorus/g of plant material was correlated with increased rates of phosphate fertilization. Significantly greater amounts of plant tissue phosphorus were present in the high phosphorus regimes than in the low phosphorus regimes with the medium phosphorus regimes being intermediate to both. At 180 days green needlegrass did not show significant differences in the amount of phosphorus present in plant tissue of any treatments.

TABLE 4. THE EFFECTS OF PHOSPHATE FERTILIZATION ON SHOOT DRY WEIGHT, P CONCENTRATION AND ROOT INFECTION LEVELS IN WESTERN WHEATGRASS (*A. smithii*)*

	Weight (g)		% Infection		µg P/g Plant Matter	
	90 days	180 days	90 days	180 days	90 days	180 days
M+ No P	7.05a	12.36ab	40.8c	75.0d	11.2ab	8.0ab
M- No P	5.21a	13.50b	0.2a	0.0a	9.6a	7.1a
M+ 25 ppm P	5.46a	13.56b	22.6b	41.0b	13.8bc	8.5ab
M- 25 ppm P	5.35a	12.01ab	0.0a	0.3a	12.8abc	7.6ab
M+ 50 ppm P	6.05ab	11.36a	5.4a	52.5c	14.7c	9.9c
M- 50 ppm P	6.08ab	11.13a	0.0a	0.0a	16.0c	9.0bc

*Values are means of 5 replicates (90 days) and 4 replicates (180 days). Means in the same column followed by at least one of the same letters are not significantly different at the 0.05 level of probability.

Big sage (*Artemisia tridentata*) was the only one of the five species tested to exhibit growth responses typically observed in VA endosymbiont associations. An increase in shoot dry weight and height was accompanied by increased phosphate uptake in big sage plants subjected to the low phosphorus regime. A lack of such fungus-induced responses was evident at higher soil phosphorus concentrations. Table 5 points out that all parameters measured were significantly greater in the M+ versus the M- treatment where no fertilizer was applied to the soil. The increase in weight, height and phosphorus between M+ and M- treatments at the No phosphorus level were readily evident visually. Weight was increased 143 percent, height 81 percent and phosphorus content 51 percent.

DISCUSSION

At least two explanations exist for the lack of mycorrhizal infection development in fourwing saltbush and winterfat. The first and most obvious is that the wrong species of fungus was used as inoculum. This is very likely as a certain amount of host/symbiont specificity is known to occur.

TABLE 5. THE EFFECTS OF PHOSPHATE FERTILIZATION ON SHOOT DRY WEIGHT, P CONCENTRATION AND ROOT INFECTION LEVELS IN BIG SAGE (*A. tridentata*)*

	Artemisia Tridentata			
	Weight (g)	Height (cm)	μg P/g Plant Mat'l	% Infection
M+ No P	1.63b	10.11b	58.1bc	62.5d
M- No P	0.67a	5.60a	38.6a	0.0a
M+ 25 ppm P	1.16ab	8.83b	69.9cd	40.8d
M- 25 ppm P	1.51b	9.84b	68.4bcd	0.0a
M+ 50 ppm P	1.32ab	9.63b	57.1b	11.0b
M- 50 ppm P	1.17ab	7.97ab	70.4d	0.0a

*Values are means of 8 replicates. Means in the same column followed by at least one of the same letters are not significantly different at 0.05 level of probability.

Lindsey, Cress and Aldon[16] found no infection in fourwing saltbush inoculated with *G. fasciculatus*. *G. mosseae* was the endosymbiont found by Williams and Aldon[12] to increase growth of fourwing saltbush. A second explanation has to do with a host plant mechanism suggested by Woolhouse[17] which might allow the plant to guard against infection by VA mycorrhizae when phosphate is adequate. Since neither species responded to the addition of phosphate, this, too, may explain the lack of infection in fourwing and winterfat. Whatever the case, more studies need to be carried out before anything definitive may be concluded as to the nature of the relationship between mycorrhizal fungi and members Chenopodiaceae.

Green needlegrass and western wheatgrass developed mycorrhizal infections, but no persistent increases in biomass occurred. It would appear that endosymbiont effectiveness rather than specificity was the critical factor in the grasses tested. Although the fungus did not aid the grasses in the uptake of phosphate, the relationship did not degenerate to one of host/pathogen. Thus, although plant growth was not increased, neither was it decreased by the presence of G. fasciculatus. Certain interactions between the grass plants and the fungus remain unexplained and will require more research. The possibility exists that the fungus actually increased root biomass. Since separation of very fine roots from the compacted soil was not effected, any measurement of root biomass would have provided a very inaccurate approximation. Therefore, none was attempted.

Significant increases in biomass, height and phosphorus content were observed in the M+, low phosphorus treatment of big sage. The strain of endosymbiont with which all species were inoculated was originally taken from soil beneath big sage. This may account for the fact that the only persistant positive response to VA endosymbiont infection was exhibited by big sage. The general consensus of research done in recent years is that certain endosymbiont strains are indeed more effective in phosphorus uptake (and thus growth stimulation) than others (Jackson, Franklin and Miller;[18] Mosse;[19] Powell[20 21]). The specificity and varying effectiveness of fungal endosymbionts found in association with native plants may therefore regulate the extent of plant growth enhancement and nutrient uptake.

The findings of this study do not conclusively prove that VA mycorrhizae are essential to the establishment of stable ecosystems, but it is essential that microbiological aspects of ecosystems be evaluated along with aboveground vegetation. Without such evaluations reestablishment of truly stable ecosystems may never be assured. More studies of this nature may reveal the presence of a variety of endosymbiotic fungi which infect a variety of species. Should this prove to be the case, the need for phosphate fertilization on disturbed areas could be greatly reduced by intensive soil management and maintenance of mycorrhizal populations.

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THE EFFECT OF RETORTED OIL SHALE ON VA MYCORRHIZA FORMATION IN SOIL FROM THE PICEANCE BASIN OF NORTHWESTERN COLORADO

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INTRODUCTION

Processing of oil shale in northwestern Colorado for recovery of fuel oil will result in the generation of vast amounts of waste retorted shale. Cundell[1] estimated that the minimum sized economically feasible shale plant would generate about 50,000 tons of waste shale per day. Although improved technology may reduce this figure, the disposal of waste shale will present a major problem in reclamation since these wastes have a number of properties detrimental to plant growth. For example, these wastes are highly alkaline (pH = 9 - 10), are deficient in nitrogen and phosphorus, and have a very high sodium content (Schmell and McCaslin,[2] Cundell,[1] Redente[3]). In addition most of the heavy metals contained in oil shale are retained in the solid wastes (Shendrikar[4]), and the fine texture of the wastes is unfavorable to water infiltration and aeration.

Schmell and McCaslin[2] have shown that when oil shale wastes comprised more than 50% of a soil-shale mixture, growth of Russian wild rye (*Elymus junceus*) and Alkar tall wheat grass (*Agropyron elongatum*) was severly reduced. Microbial activity, as measured by ATP concentrations and by nonsymbiotic nitrogen fixation, has also been shown to be reduced by increasing amounts of retorted oil shale added to soil (Klein[5]). Although the activity of both ecto-and endo-mycorrhizal fungi has been investigated on coal wastes (Schram,[6] Daft and Nicholson,[7] Daft, Hacskaylo, and Nicholson,[8] Marx,[9] Khan[10]) little is known about the effects of oil shale wastes on mycorrhiza formation. Since the presence of mycorrhizal associations has been shown to be beneficial to the growth of many plant species (Gerdemann,[11] Mosse[12]), including species native to northwestern Colorado (Aldon,[13] Kiel[14]), and appears to be an important factor in revegetation of disturbed lands (Reeves et al.,[15] Moorman and Reeves[16]) the effect of adding oil shale wastes to topsoil on mycorrhiza formation must be considered. This paper reports the results of experiments designed to test the effect of retorted oil shale amendments to topsoil on the formation of mycorrhizae using corn as a test plant.

METHODS

Paraho retorted oil shale used in this study was obtained from oil shale succession plots in the Piceance Basin in Rio Blanco County and the topsoil tested was collected from the surrounding midelevation sage community. Collections for the two replicates used in this study were made in June and October, 1978.

For each replicate, mixtures of soil and retorted shale were prepared in the following V:V proportions: 10, 25, 50, and 75% retorted shale along with controls of 100% retorted shale and 100% soil. Since retorted oil shale contains no viable propagules of mycorrhizal fungi it can affect mycorrhiza formation when added to the soil in two ways: (1) by acting as a dilutant of propagules present in the soil and, (2) by physically and/or chemically altering the soil. To separate the physical/chemical effects from dilution effects, mixtures of soil and sand in proportions corresponding to the soil-shale proportions were prepared. Each mixture was then used to fill five disinfected 400 ml pots. Surface sterilized corn seeds were planted in each pot and grown in the greenhouse for 30 days. At the end of this growing period the corn plants were uprooted and 100 1 cm sections of each root system were randomly selected, stained, and assessed for relative degree of mycorrhizal infection following the method of Phillips and Hayman.[17]

Comparisons were made of average percent infection in each treatment using a two-way analysis of variance for each replicate and for the combined data of the two replicates.

In a second set of experiments oil shale was mixed with autoclaved topsoil in the same proportions as in the previous experiment. Equal volumes of sand from pot cultures of a mycorrhizal symbiont (*Glomus fasciculatus*) on corn were then added to each mixture to serve as an inoculum of mycorrhizal fungi. Since equal inoculum was added to each treatment in this study, any change in mycorrhiza formation could be attributed to properties of the shale *per se* rather than dilution. Four corn plants were grown in each mixture for 30 days in the greenhouse, then uprooted and assessed for relative amounts of mycorrhizal infection in each treatment, as in the previous experiment. Two replicates were done of this study, one in November, 1978, and the second in February, 1979, both using soil and shale collected in October, 1978.

RESULTS

The average percent infection and range of percent infection for the five plants in each treatment in both replicates are shown in Table 1. Mixtures of up to 25% sand or oil shale did not decrease mycorrhizal infection compared to the undiluted soil. As the amount of amendment increased beyond 25% however, the average amount of mycorrhiza formation decreased, with the oil shale mixtures decreasing more rapidly than the sand mixtures. In the first replicate the percent infection for both the sand and the oil shale mixtures decreased significantly at $\alpha = 0.1$ as the percent amendment

TABLE 1. PERCENT VA MYCORRHIZAL INFECTION IN CORN ROOTS GROWN IN SOIL-SAND OR SOIL-OIL SHALE MIXTURES

First Replicate

Percent Amendment	Percent Infection			
	Sand		Oil Shale	
	Ave. %	Range %	Ave. %	Range %
10	91	84-98	93	88-100
25	93	84-100	86	80-92
50	60	48-70	46	0-88
75	47	42-52	18	12-24
100	0	0	0	0
None	Ave. = 87% Range: 72-96%			

Second Replicate

Percent Amendment	Percent Infection			
	Sand		Oil Shale	
	Ave. %	Range %	Ave. %	Range %
10	66	61-75	93	84-97
25	64	55-75	83	75-90
50	69	61-76	49	11-69
75	37	24-53	13	4-24
100	0	0	0	0
None	Ave. = 78% Range: 57-88%			

increased but there was no significant difference between the sand and the oil shale amended soils. In the second replicate both the 50% and the 75% oil shale mixtures showed significantly less infection than the unamended soil at $\alpha = 0.05$, while the sand mixtures showed no significant decrease until sand comprised 75% or more of the mixture. Also of interest is the great variation in percent infection in the five plants in each of the 50% oil shale treatments compared to the other treatments. The comparatively wide range of values at this point may indicate that 50% oil shale was near the threshold of tolerance for mycorrhiza formation so that small variations between samples at this point created large differences in mycorrhiza formation.

Figures 1 and 2 show the results of this experiment graphically. Figure 1 shows the percent infection plotted against percent amendment for the individual replicates, and Figure 2 shows the averages of the two replicates combined. Both figures show little effect of dilution by sand on mycorrhiza formation until it exceeds 25% to 50% of the substrate. The decrease in mycorrhiza formation is more pronounced when retorted oil shale is added to soil than when an equal volume of sand is added, indicating that the effect of retorted oil shale cannot be attributed solely to dilution of propagules.

The results of the second study, in which sterile mixtures were reinoculated with equal amounts of propagules, are shown in Table 2 and Figure 3. In both replicates mycorrhiza formation was inhibited when retorted oil shale comprised more than 50% of the substrate. However, the mixtures with lesser amounts of oil shale gave more equivocal results. In the first replicate small amounts of retorted shale appeared to enhance mycorrhiza formation, while the second replicate did not show this effect. Because of these differences at low concentrations of retorted shale, one way analysis of variance failed to show significant decreases in mycorrhiza formation as the concentration of oil shale increased. However, the linear correlation between percent infection and percent retorted oil shale of -0.52 was significant at $\alpha = 0.01$, indicating that there is some relationship between the two factors.

TABLE 2. PERCENT VA MYCORRHIZAL INFECTION IN CORN ROOTS GROWN IN REINOCULATED AUTOCLAVED SOIL-OIL SHALE MIXTURES

Percent Amendment	Percent Infection			
	Rep. 1		Rep. 2	
	Ave. %	Range %	Ave. %	Range %
0	33	11-48	38	14-50
10	55	44-65	27	19-33
25	46	25-61	39	26-63
50	36	23-60	17	15-20
75	17	1-51	6	4-10
Uninoc. Soil	0	0	0	0
Unioc. Oil Shale	0	0	0	0

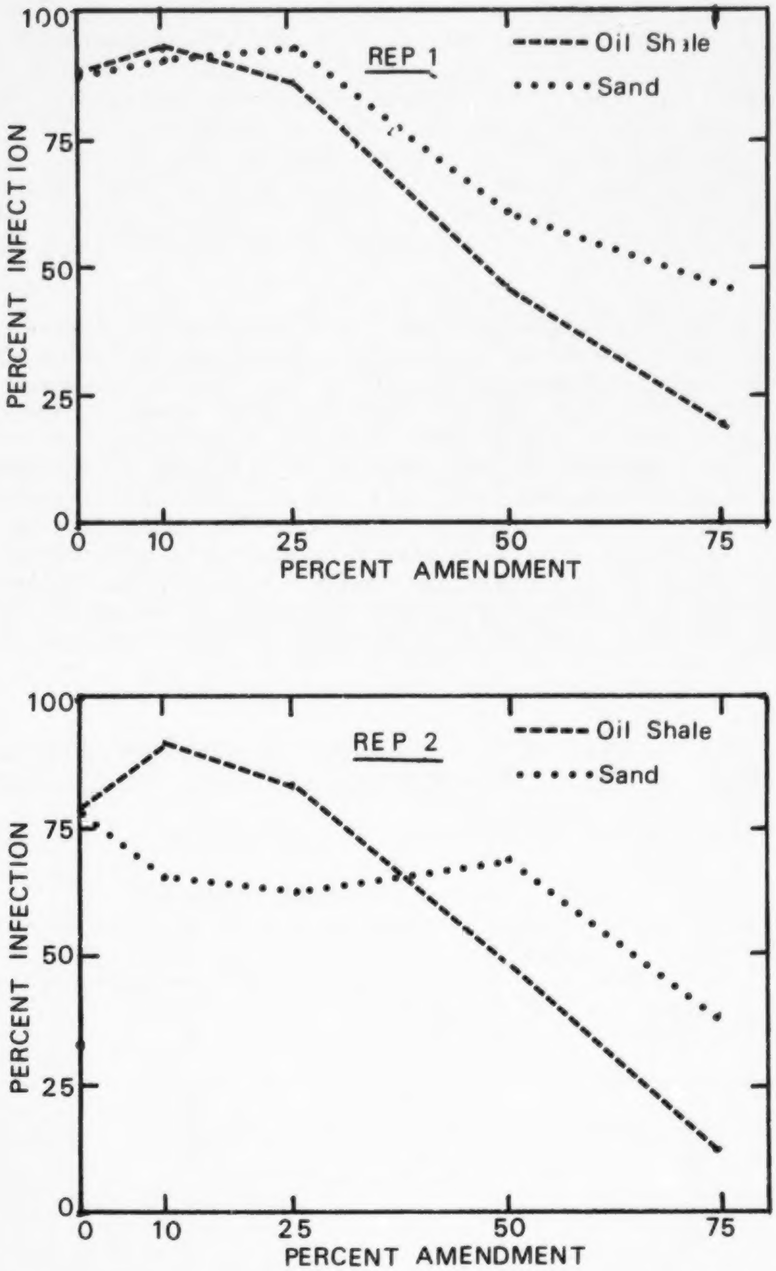

Figure 1: Percent VA mycorrhizal infection in corn roots grown in soil amended with various amounts of retorted oil shale or sand.

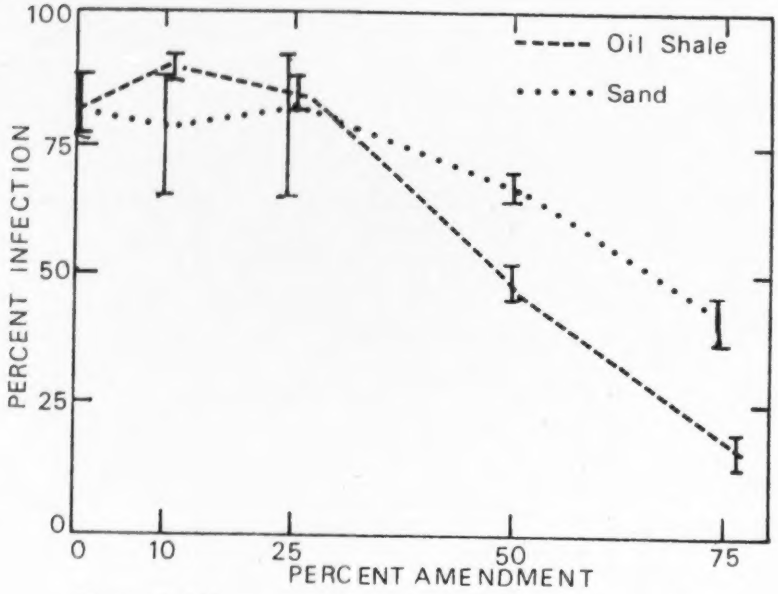

Figure 2. Percent VA mycorrhizal infection in corn roots grown in soil amended with various amounts of sand or retorted oil shale, averages and ranges of two replicates.

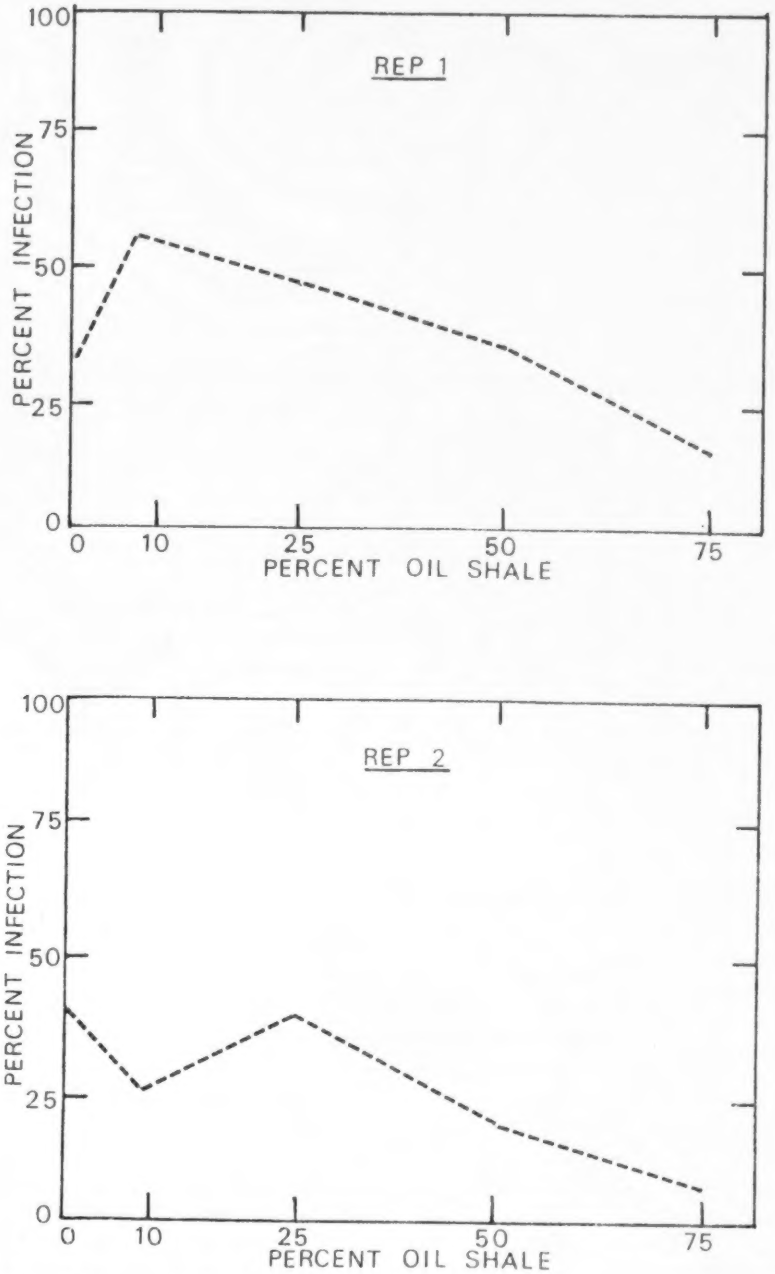

Figure 3. Percent VA mycorrhizal infection in corn roots grown in autoclaved soil amended with various amounts of retorted oil shale and reinoculated with equal amounts of propagules of mycorrhizal fungi.

DISCUSSION

Mycorrhizae have been shown to be an integral part of virtually all plant communities (Mosse,[12] Gerdemann[11]) and reduction in the potential of the soil to form these associations due to various types of disturbance has been shown to be correlated with often undesirable changes in vegetation (Reeves et al.,[15] Moorman and Reeves[16]). The data presented in this paper suggest that mixing large quantities of untreated retorted oil shale with topsoil can reduce the formation of mycorrhizal associations in plants growing in that soil. Further studies to determine how various treatments of shale can affect mycorrhiza formation should provide valuable information for revegetation of lands involved in retorted shale disposal. For example, we are currently monitoring a series of oil shale succession plots to determine how burying shale under different depths of soil will affect mycorrhiza formation. Other studies on shale that has been leached or otherwise treated could also provide useful data.

In addition, long term studies on the effect of oil shale wastes on mycorrhizal activity should be initiated. Presently there are many unanswered questions about the nature of the inhibitory effects of retorted shale on mycorrhiza formation. For example, we do not know if factors in the shale kill the fungal symbiont or merely retard its growth, nor do we know if the inhibition of mycorrhiza formation can be overcome by increasing inoculum density.

The composition and activity of the soil microflora has been shown to be influenced by soil pH, water potential, organic matter, degree of disturbance, and presence of heavy metals (Brown,[18] Griffin,[19] Wei-chu and Griffin,[20] Ruhling and Tyler,[21] Jordan and LeChevalier,[22] Lawrey[23]) and selection of microbial strains tolerant to heavy metals has been observed in the lab and in nature (Ross,[24] Jordan and LeChevalier[22]). Some evidence of different strains or species of mycorrhizal fungi being limited to specific soils also exists (Worley and Hacskaylo,[25] Mexal and Reid,[26] Daft and Nicholson,[7] Kruckelmann,[27] Abbot and Tobson,[28] Johnson,[29] Powell[30]). Changes in soil properties due to addition of oil shale wastes could, therefore, lead to selection of certain tolerant strains and elimination of other strains. Since some host specificity has been observed with mycorrhizal fungi (Mosse[31]) selection of certain strains of fungi could influence which host plants can become successfully established on lands affected by oil shale waste disposal.

All of these problems offer fruitful areas for further research. Such research will require carefully controlled means of comparing mycorrhizal populations in various soils. The type of bioassay used in this study and described in the previous paper offers a relatively easy and fast means of comparing the mycorrhizal potential of different soils or treatments. However, work in our lab and others suggests that light intensity and quality, temperature, and watering regimes can affect the results of a bioassay of this type. Therefore, it is essential that bioassays for mycorrhizal potential be done under standardized, defined, and easily reproducible conditions. Research is currently underway in our lab to better determine how various environmental variables can affect the results of mycorrhizal bioassays.

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APPENDIX A

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